Environmental Sciences Laboratory

Performance Assessment and Recommendations for Rejuvenation of a Permeable Reactive Barrier: Cotter Corporation's Canon City, Colorado, Uranium Mill

April 2005

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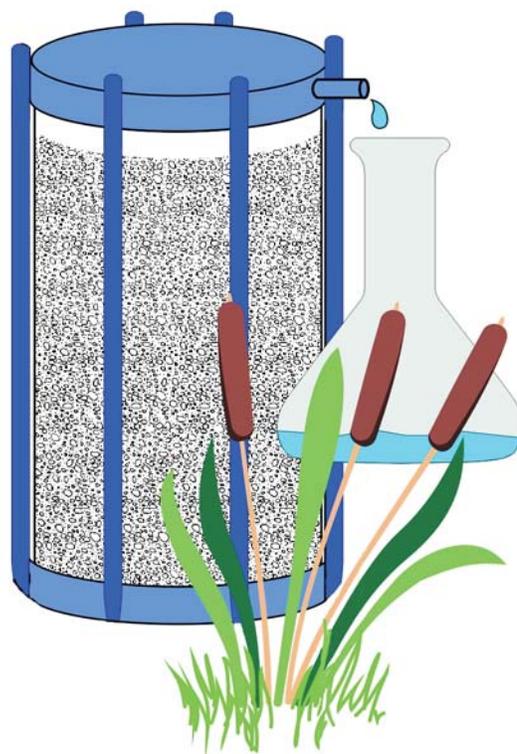
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Executive Summary

Permeable reactive barriers (PRBs) are zones of reactive materials designed to passively treat contaminated ground water. In June 2000, construction was completed on a PRB at a uranium-ore milling site operated by Cotter Corporation (Cotter) near Canon City, Colorado. The PRB uses zero-valent iron (ZVI) as the reactive medium and is intended to mitigate molybdenum and uranium contamination in ground water. The PRB has not functioned as well as expected and the objective of the current study was to determine possible causes for the early breakthrough of molybdenum.

The Cotter PRB consists of a 30-ft wide (perpendicular to direction of ground-water flow), 5-ft long (in the direction of ground-water flow), reactive zone containing 80 tons of Peerless –8 + 50 mesh ZVI. Sand zones, 2 ft in length, were placed hydraulically up-gradient and down-gradient of the ZVI zone. Hypalon funnel walls approximately 370 ft in length direct ground water to the reactive zone. Ground-water flux is about 1 gal/min but may have been as high as 3 gal/min at times. At 1 gal/min, the residence time[1] was initially about 56 h and 2,036 pore volumes[2] would have passed through the PRB prior to this investigation.

Mean concentrations of molybdenum and uranium in the untreated ground water are 4.8 and 1.0 mg/L, respectively. Initially (from June 2000), the PRB functioned effectively, with mean molybdenum concentrations less than 0.2 mg/L and mean uranium concentrations less than 0.01 mg/L in ground-water samples from the ZVI zone. In April 2001, mean molybdenum concentrations in ZVI samples had increased but were still less than 1.0 mg/L, and uranium concentrations remained less than 0.01 mg/L. After less than 1 year of operation, molybdenum concentrations in ground water contacting the ZVI increased significantly, suggesting that the PRB was no longer treating molybdenum effectively. By January 2003, molybdenum concentrations in ZVI samples exceeded the incoming concentrations and values up to 19 mg/L were observed. On the basis of the assumed ground-water flux of 1 gal/min, the ZVI treated only about 200 pore volumes of ground water before the molybdenum concentrations began increasing. Coincident with the increase in effluent molybdenum concentrations was an increase in ground-water elevation in the subsurface sand upgradient of the PRB (mounding). In contrast, uranium in the ZVI zone had remained at concentrations less than 0.006 mg/L.

Sampling results of dissolved constituents indicate that ground water initially flowed through and was treated by the ZVI, but by November 2003, sampling results in the down-gradient sand indicated that some ground water bypassed the ZVI. By October 2004 nearly all ground water was bypassing the PRB or was flowing through preferential pathways and not being treated. Mounding of the ground-water table in the upgradient sand was coincident with changing of the ground-water chemistry and indicates decreasing hydraulic conductivity.

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[1]In this report, residence time refers to the average length of time that a particle of water remains in contact with the ZVI. It is estimated as the length of time required for one pore volume of fluid to pass through the ZVI. Residence time is a convenient unit for normalizing data so that results of a large-scale test, such as a field PRB, can be compared to a small-scale bench test, such as a column experiment

[2]In this report, a pore volume is defined as the volume of fluid in contact with ZVI at a given time. It is estimated by the volume of water required to fill the pore space. Pore volume is a convenient unit for normalizing data so that results of a large-scale test, such as a field PRB, can be compared to a small-scale bench test, such as a column experiment

In October 2004, a field investigation was initiated to explore the causes of the increasing molybdenum concentrations and the mounding of ground water. The west end of the PRB was exposed by excavation to provide direct observation of the ZVI. Upgradient and downgradient sand zones were unaltered and appeared much the same as when they were installed, but the ZVI had cemented since installation. The rigidity of the ZVI indicated the presence of mineral precipitants.

Samples of the ZVI were analyzed for bulk (total) chemistry. Concentrations of solid-phase uranium ranged from less than 5 to 3,727 μg/g, and nearly all the uranium is within 0.5 ft of the front face of the ZVI. Uranium concentrations are high from the base of the ZVI to the 5-ft level and are low in the 6- and 7-ft levels, suggesting that the ground-water table reached a maximum height of about 5 ft. Concentrations of solid-phase molybdenum range from less than 130 to 4,050 μg/g. Molybdenum concentrations are also greatest in samples collected within 0.5 ft of the upgradient edge of the ZVI. However, unlike uranium, molybdenum concentrations are significantly greater than background concentrations well into the ZVI. Solid-phase calcium concentrations range from less than 5 μg/g to 44,200 μg/g and are highest within 0.5 ft of the front; however, calcium is present in high concentrations throughout most of the ZVI zone. Calcium resides in calcium carbonate minerals that occupy up to 20% of the available porosity.

Petrography and electron microscopy methods were utilized to further evaluate the mineralogy and texture in samples from the Cotter PRB. Calcium carbonate is ubiquitous throughout the ZVI, occurring as bladed crystals. The crystals often coat ZVI grains and reduce porosity. Iron oxides are also prevalent and further decrease porosity. Sulfide minerals overlie and intermix with calcium carbonate and iron oxides. Corrosion products often form bands more than 100 μm thick and cause significant porosity reduction. High solid-phase concentrations of molybdenum and uranium are often associated with sulfide mineralization and indicate the presence of distinct molybdenum and uranium mineral phases. Bench-scale tests were made of several treatments to determine if the corrosion minerals, particularly calcium carbonates and iron oxides, could be removed chemically. Weak (10%) hydrochloric acid removed the corrosion products and appears to have restored the ZVI to its original state.

A column test was conducted to determine if ZVI from the Cotter PRB is still reactive for uptake of molybdenum and uranium and to evaluate mineral precipitation. The test used friable ZVI sampled from the PRB and a synthetic ground water mimicking ground water upgradient of the PRB. With 8 hours of residence time, molybdenum was effectively removed for the duration of the test, nearly 200 pore volumes. However, when the residence time was shortened to less than 0.5 hours, less molybdenum was removed. When the column was subjected to pH values exceeding 10, molybdenum concentrations in the effluent were higher than those in the influent. Uranium concentrations in column effluents were low regardless of residence time or pH values. Flow to the column was discontinued for several days; following this shutdown, sulfate reduction was observed and was aided by sulfate reducing bacteria. Effluent calcium and iron concentrations decreased with increased residence time, consistent with previous studies of geochemistry in ZVI-based PRBs.

Chemical and hydrologic results of the Cotter PRB are explained by a conceptual model involving four distinct chemical stages. During Stage 1, molybdenum was efficiently removed from the ground water, resulting in effluent concentrations of less than 0.2 mg/L. The water table (piezometric surface) was flat across the ZVI and both sand zones. Stage 1 is characterized by

flow through the porous media flow in the PRB. During Stage 2, molybdenum concentrations in the ZVI steadily increased from less than 0.2 to about 4 mg/L. Water levels were flat across the ZVI and the downgradient sand, but the level in the upgradient sand increased by about 1 ft above the level in the ZVI. Stage 2 is characterized by an initial development of preferential flow paths that decreased the residence time of the ground water in the ZVI. During Stage 3, molybdenum concentrations in the ZVI were relatively constant between about 2 and 4 mg/L. The elevation of the water table in the upgradient sand increased rapidly (mounding) and reached a maximum of about 4 ft above the water level in the ZVI. Preferential flow through the ZVI continued through Stage 3.

In Stage 4, molybdenum concentrations in the ZVI increased to as high as 19 mg/L in response to pH values of more than 10. Molybdenum that was previously precipitated was redissolved. Ground water bypassed the ZVI in Stage 4 and was nearly stagnant within the ZVI, yielding lengthy residence times. The ground-water level in the ZVI increased to about 2 ft above the level in the downgradient sand, indicating that hydraulic conductivity in the ZVI was decreasing. Chemical indicators of long residence in the ZVI include calcium and magnesium concentrations nearly zero, and pH values of more than 10. Also in Stage 4, sulfate concentrations in the ZVI were much lower than in the incoming (influent) ground water because of precipitation of sulfide minerals.

Recommendations for improving the efficiency of the Cotter PRB include the following considerations: (1) install an accessible treatment system that can be easily monitored and modified, (2) flush the existing PRB with weak acid to restore hydraulic conductivity, and/or (3) install a pretreatment zone consisting of coarse gravel mixed with ZVI. Although not specifically tested, we do not believe that ultrasonication would be an efficient means of restoring the functionality of the PRB.

This investigation also reviewed all other projects in which ZVI is known to have been used to remediate molybdenum. The other project sites are former uranium-ore milling sites near Durango, Colorado, and Monticello, Utah. Data from these projects suggest that molybdenum is removed from solution by ZVI but that the reaction is slower than for uranium removal. Thermodynamic considerations indicate molybdenum may be precipitated as a ferrous molybdate mineral. At Durango, ZVI treated molybdenum for about 400 pore volumes, after which concentrations began to increase. The PRB at Monticello appears to have treated molybdenum for at least 900 pore volumes. Evidence from column tests associated with the Monticello PRB project confirm ZVI removes molybdenum, but the rate of removal is less than for uranium.

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1.0   Introduction

Permeable reactive barriers (PRBs) are zones of reactive materials designed to passively treat ground water and are rapidly becoming one of the most widely used means of remediating ground water. PRB remediation technology is relatively new; the first commercial field installation was completed in 1994 (Warner et al. 1998). Since that time, more than 70 PRBs have been constructed. Many of these contain granular zero-valent iron (ZVI) as the reactive material. ZVI causes reduction of chlorinated volatile organic contaminants to nontoxic constituents (Gavaskar et al. 1998). ZVI also fixes metals and radionuclides by precipitating immobile solid materials (Morrison et al. 2002d). The corrosion of ZVI leads to lowered oxidation states, which cause chemical reduction of some contaminants.

In June 2000, construction was completed on a PRB at a uranium-ore milling site operated by Cotter Corporation (Cotter) near Canon City, Colorado (Niesen 2000a). The PRB uses ZVI as the reactive medium and is intended to mitigate contamination of molybdenum (Mo) and uranium (U) dissolved in ground water. Mean concentrations of Mo and U in the untreated ground water for the period November 2001 through October 2004 are 4.8 and 1.0 mg/L, respectively. The PRB functioned well initially, with mean Mo concentrations in samples from the ZVI zone less than 0.2 mg/L and U concentrations less than 0.01 mg/L (Niesen 2000a). Through about April 2001, mean Mo concentrations in ZVI samples were less than 1.0 mg/L and U concentrations continued to remain less than 0.01 mg/L.

After less than 1 year of operation, Mo concentrations in ZVI samples began increasing, suggesting that the PRB was failing to remove Mo. By January 2003, Mo concentrations in the ZVI samples exceeded the incoming concentrations, and values to 19 mg/L were observed in the ZVI samples. Coincident with the increase in Mo concentration was an increase in the ground-water elevation upgradient of the PRB. In January 2004, as a corrective action, ground water upgradient of the PRB was pumped back to a tailings pond on the mill site to minimize the mounding of ground water near the PRB. Most uranium concentrations in ZVI zone samples have remained at less than 0.01 mg/L.

2.0   Background: Other Studies of Molybdenum Uptake by Zero-Valent Iron

This section presents summaries of all other projects we are aware of that investigated the uptake of Mo by ZVI. Project sites are near Durango, Colorado, and Monticello, Utah.

2.1 Molybdenum Uptake by Permeable Reactive Barriers at the Durango, Colorado, Site

In 1996, a PRB using a baffled tank (similar to some septic tanks) was constructed to treat contamination in leachate from a U mill tailings disposal site located near Durango, Colorado (Morrison et al., 2002b). The tank measured 3 ft wide, 6 ft long, and 4.2 ft high; ZVI was used as the reactive medium. The PRB initially contained foamed ZVI bricks (manufactured by Cercona of America, Dayton, Ohio), but, the foamed ZVI was replaced with Peerless –8 + 20 mesh granular ZVI in 1999.

The incoming concentration of Mo (about 1 mg/L) was less than the influent concentration at the Cotter PRB site. Both types of ZVI removed Mo from the disposal cell leachate, but both types showed increasing concentrations in the effluents after several hundred pore volumes (Figure 1). In contrast, U concentrations in the effluents typically remained less than 0.01 mg/L throughout the operation of the PRBs. Calcium concentrations decreased only by about 10% across the PRB in samples of both ZVI media and pH values increased from about 6.7 to 7.4.
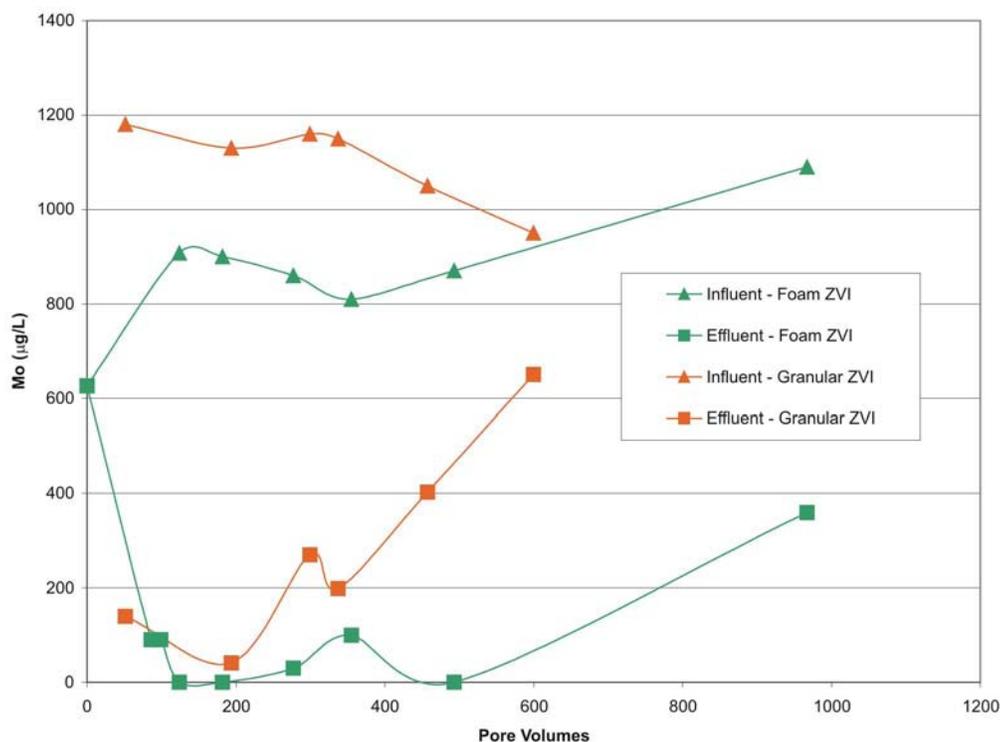
Figure 1. Mo concentrations in two Durango treatment cells containing foam ZVI blocks and granular ZVI

2.2 Molybdenum Uptake in the Monticello, Utah, Permeable Reactive Barrier

In 1999, an in situ PRB containing ZVI was installed downgradient of a former U mill tailings site near Monticello, Utah (Morrison et al. 2002a). This PRB has three zones. The furthest upgradient zone (the "pretreatment" zone) has 13% ZVI by volume mixed with pea gravel. Just downgradient from the "pretreatment zone" is a zone of 100% ZVI, followed by the third zone containing 100% gravel and an air sparging unit.

Contaminated ground water flows through alluvium in the mid-portion of an erosional valley. The alluvium is underlain by low-permeability bedrock composed of siltstone and shale. The PRB is keyed into the bedrock to prevent ground water from underflowing the reactive material. Soil-bentonite slurry walls direct ground water to the PRB and are also keyed into the bedrock. The slurry walls extend south and north of the PRB and were designed to extend to the valley walls, thus, directing the entire alluvial ground-water system to the PRB.

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Although the PRB was principally constructed primarily to remediate U contamination, Mo concentration data have also been collected since installation. Influent concentrations of Mo normally range from 0.025 to 0.045 mg/L (Figure 2). Effluent concentrations range from 0.0004 to about 0.005 mg/L, indicating that Mo is being treated by the ZVI.
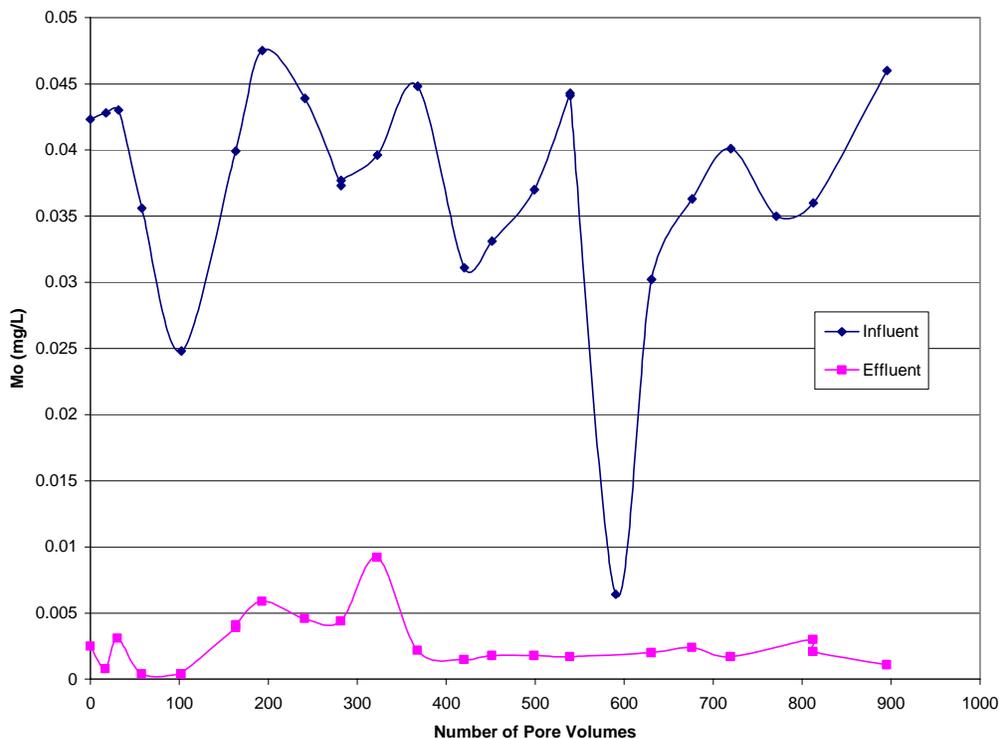
Figure 2. Dissolved Mo concentrations in influent and effluent ground water samples at the Monticello PRB for a typical well transect

2.3 Molybdenum Uptake in the Monticello, Utah, Permeable Reactive Barrier: Bench-Scale Tests

Prior to construction of the Monticello PRB, several bench-scale studies were conducted to measure Mo. The results are informative in understanding Mo reactivity with ZVI.

2.3.1 Small Column Tests

Twelve column tests were conducted in glass chromatographic columns. ZVI or admixtures of ZVI with pH buffers were placed in each column (Table 1). Dimensions of the columns were 150 mm long by 15 mm diameter. Ground water from the contaminated plume (well 92-11 located upgradient from the PRB location) was introduced into the bottom of each column. The flow rate was about 0.10 mL/min, resulting in a residence time of about 2 h. Columns were operated for about 100 to 250 pore volumes of ground water. MACTEC (1998b) provides more details of the experimental methods and complete results.

Results indicate that most forms of ZVI were able to significantly reduce the concentrations of dissolved Mo, but pH values are an important factor in Mo uptake by ZVI. The two tests that

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included magnesium hydroxide [$Mg(OH)_2$] had pH values of more than 9.3 and also had the highest concentrations of Mo in samples of the column effluents (tests 1 and 2, Table 1). The correlation of high Mo concentrations with high pH values is due either to the higher solubility of Mo-bearing minerals at high pH values or to a lower capacity for adsorption to oxide mineral surfaces. These same two tests also had the lowest concentrations of iron dissolved in the effluents (Table 1), probably because of the formation of ferrous hydroxide at the elevated pH values. Low dissolved ferrous Fe concentrations would prevent precipitation of ferrous molybdate and could result in increased concentrations of dissolved Mo (Morrison et al. 2002c).

Table 1. Results of treatability column tests for Monticello PRB project listed in order of Mo concentration in column effluent. All values are from the final sampling of the column, representing between about 100 and 250 pore volumes.

Test No.	ZVI Brand and Admixture Composition	pH	Mo (mg/L)	Fe (mg/L)
Influent	Well 92-11 ground water	7.85	0.2	0.026
1	Cercona HSA, High $Mg(OH)_2$	9.33	0.184	0.01
2	Peerless -8 + 50 (50%), $Mg(OH)_2$ (50%)	9.42	0.173	0.048
3	Peerless (50%), concrete (50%)	7.7	0.08	7.2
4	Cercona cast iron -3 +20	8.12	0.066	8.13
5	Peerless (50%), limestone (50%)	7.98	0.058	8.47
6	Peerless -8 +50 (50%), dolomite (50%)	8.08	0.054	9.91
7	Peerless (50%), cement (50%)	8.02	0.048	10.5
8	Cercona -3 +12	8.08	0.046	6.78
9	Cercona HSA	8.01	0.031	8.18
10	Peerless -8 + 50	8.1	0.019	5.93
11	Connelly +60	8.11	0.006	5.33
12	Master Builder GX027	8.08	0.004	2.93

2.3.2 Field Treatability Tests

Column tests were conducted in a field trailer adjacent to well 88-85 at the Monticello site (upgradient of the proposed PRB site). We tested five different brands of ZVI to compare contaminant uptake efficiency. Water was pumped from well 88-85 to a holding tank and then into the columns. Columns, made of clear acrylic, were 4ft high and 4in in diameter. Flow rates typically ranged from 20 to 80 mL/min, resulting in residence times of between 1 and 4 h. One column was fitted with septa at various positions along the flow path to allow more sampling along the flow path. Flow was from bottom to top. MACTEC (1998a) provides more details of the experimental methods and complete results. The pH values of influent and all five effluents were near neutral (MACTEC 1998a). While some types of ZVI (e.g. Cercona and Connelly) appeared to remove Mo slightly better than others, all significantly reduced the concentration of Mo in the ground water (Figure 3).

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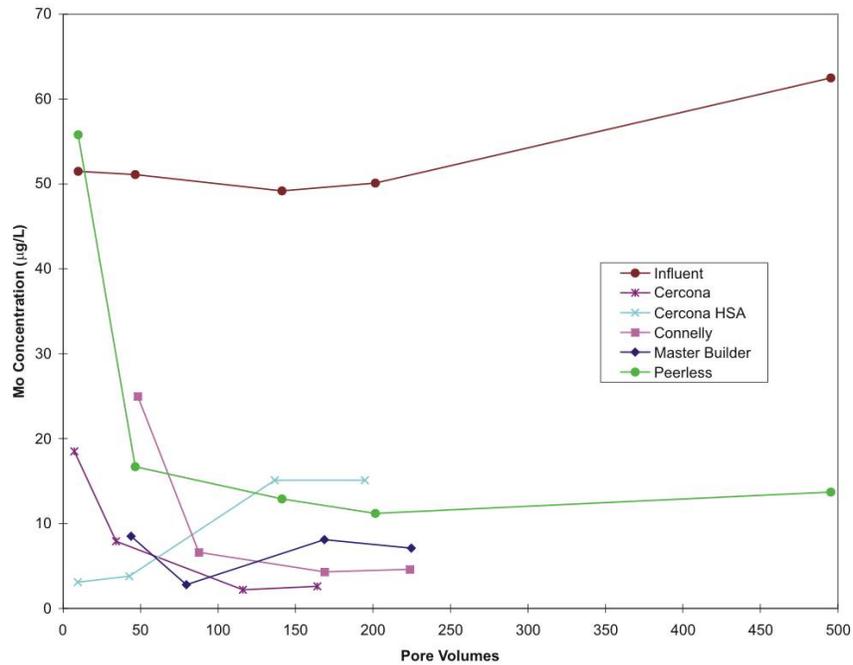
Figure 3. Effluent concentrations of Mo verses number of pore volumes passed through the columns; field treatability tests with five different brands of ZVI. All column tests were conducted identically.

One column was sampled along the flow path after 6 days of operation, equivalent to about 54 pore volumes. Concentrations of As, U, and V were less than 0.005 mg/L at the first sampling port located 2 in. from the inlet, indicating fast removal rates for these constituents. In contrast, Mo concentrations decreased more slowly, reaching a steady state value of approximately 0.016 mg/L at the third sampling port located 13 in. from the inlet (Figure 4).
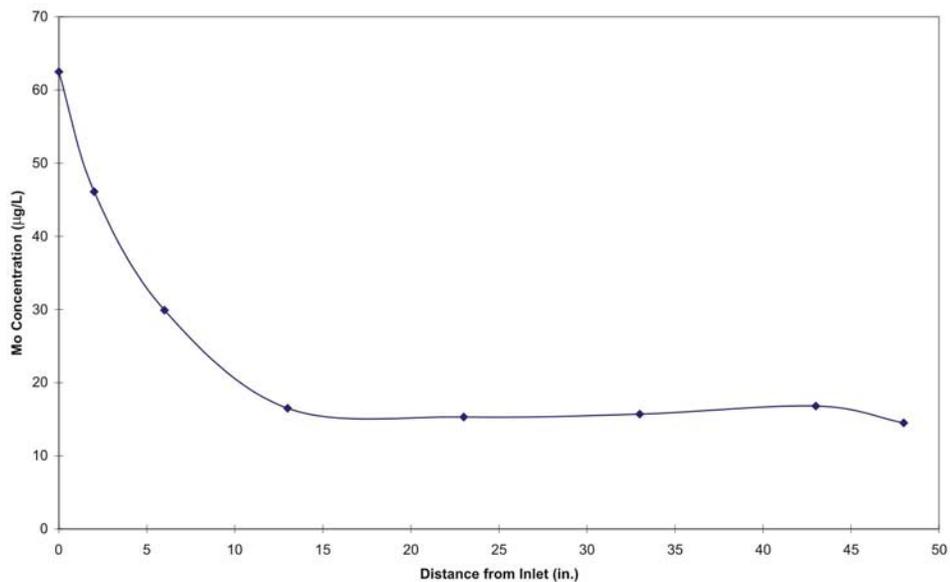
Figure 4. Profile of Mo concentrations along the column flow path after 6 days; 54 pore volumes.

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3.0   Background: Cotter PRB Site

This section provides a summary of the site hydrogeology, the results of treatability tests, and construction of the PRB system at the Cotter site. Niesen (2000a, 2000b) and Roman Z. Pyrih & Associates, Inc. (undated) provide additional details. The PRB was constructed in June 2000.

3.1   Site Geohydrology

In the area near the PRB, contaminated ground water flows through alluvium composed of unconsolidated sand, gravel, and silt (Niesen 2000a). The alluvium overlies bedrock composed of sandstone, coal, and claystone of the Vermejo Formation. Saturated thickness of the alluvium varies from less than 0.5 ft to more than 4 ft in the area of the PRB. Saturated thickness varies seasonally. Ground-water flux at the PRB site is estimated at 1 gal/min.

3.2   Treatability Testing Prior to Construction

A treatability test was conducted by Roman Z. Pyrih & Associates (undated), prior to design of the PRB system. The test used two 4-in. diameter, 4-ft-high columns. One column was filled with 23.7 kg of ZVI (ZVI column). The type of ZVI is not specified, but is assumed to be Peerless Metals Powders and Abrasives (Detroit, Michigan) –8 + 50 mesh (Peerless ZVI). The other column contained 7.4 kg of moist site alluvium in the bottom 22 in. topped with 6.8 kg of clean silica in the next 22 in. (aeration column). The pore volume of the ZVI column is estimated as 6.4 L. Flow rates varied from 4 to 5 pore volumes per day, resulting in residence times of 5 to 7 h during operation; the tests included some shutdown periods. Ground water was pumped from well 376, located near the proposed PRB site, into a holding tank and then through the ZVI column from bottom to top. Water exiting the ZVI column flowed to the top of the aeration column and passed down through the sand and alluvium. The ground water contained about 1.4 mg/L U and 8.1 mg/L Mo. Samples were collected at three sampling ports located 6, 12, and 24 in. from the base of the ZVI column and from the ZVI column effluent and the aeration column effluent.

The column tests operated for about 35 pore volumes. The ZVI column was effective at removing U from the ground water for the duration of the test. Uranium concentrations were reduced from 1.4 mg/L in the influent to less than 0.001 mg/L in the effluent. Most of the U was removed before the first sampling port, corresponding to a residence time of less than 43 min. The ZVI column was also effective at removing Mo for the duration of the test, but significantly greater residence time was required for Mo than was required for U. Molybdenum concentrations were typically reduced from 8.1 mg/L in the influent to less than 0.5 mg/L in the effluent; however, the entire column of ZVI, corresponding to residence time of about 5 h, was required for this extent of removal. Loss of Ca and bicarbonate indicate that $CaCO_3$ minerals had precipitated in the column, but this precipitation did not affect hydraulic conductivity. Dissolved Fe concentrations to 30 mg/L indicated that ZVI was dissolving.

3.3   PRB Design and Construction

The PRB and funnel walls capture nearly all of the contaminated ground water in the alluvium. Standard reliable construction techniques were used to construct this PRB in an open excavation. The PRB consists of a 5-ft-long (in the direction of ground-water flow) zone of Peerless ZVI

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with a 2-ft-long zone of clean silica sand (-8 +12 mesh) on each side. The PRB is 30 ft wide (direction perpendicular to ground-water flow) and 7 ft high. Depth from ground surface to the bottom of the PRB is about 25 ft. Each end of the PRB is supported by a vertical concrete wall. The ZVI zone contains approximately 80 tons of ZVI and is keyed into bedrock composed of claystone and coal.

Funnel walls extend 285 ft to the west and 85 ft to the east. The 36-mil Hypalon is glued to the concrete side walls of the funnel walls and is keyed approximately 3 ft into the underlying claystone/coal of the Vermejo Formation.

Construction of the PRB and funnel walls was accomplished in five steps: (1) removal of overburden soils and approximately 3 ft of claystone bedrock, (2) construction of concrete side walls, (3) construction of Hypalon wing walls, (4) emplacement of sand and ZVI, and (5) replacement of the overburden soils. After the overburden was removed, standard concrete forms were used to construct the side walls. The wing walls were completed by welding the Hypalon to the concrete side walls. Forms contained the sand and ZVI as they were poured into an open space between the concrete side walls. The forms were then removed, and the overburden soils were replaced. Ground water was pumped from the excavation during construction.

On the basis of information in Cotter's reports (Niesen 2000a, 2000b), estimates were made of various parameters that are used in this report:

Parameter	Value
Time from PRB start (June 2000) to excavation (October 2004)	4.4 yr (1591 days)
Porosity of ZVI (assumed)	50%
Volume of ZVI Zone	1,050 ft^3 (7,854 gal)
Average thickness of saturated ZVI	3 ft
Volume of saturated ZVI zone	450 ft^3 (3,366 gal)
Volume of pores (pore volume) in saturated ZVI	225 ft^3 (1,683 gal)
Average ground-water flow rate through PRB	1.0 gal/min
Average residence time at 1 gal/min	56 h
Volume of ground water treated by PRB prior to October 2005	3.43 e6 gal
Average upgradient U concentration	1.5 mg/L
Average upgradient Mo concentration	10.6 mg/L

4.0   Cotter PRB Ground-Water Chemistry and Ground-Water Elevation Trends

From installation in June 2000 through January 2001, average Mo concentrations were less than 0.2 mg/L in the ZVI samples (Niesen 2000a). By February 2001 (8 months after startup), average Mo concentrations in the ZVI samples were 1 mg/L and concentrations continued to increase. On the basis of an estimated ground-water flux of 1 gal/min, the ZVI treated an estimated 200 pore volumes of ground water before the Mo concentrations began increasing.

Chemical trends in ground-water chemistry are used in this study to help understand ground-water flux rates through the PRB since November 2001 when detailed chemical analyses were initiated. In the November 2001 ground-water sampling, dissolved Mo concentrations in samples

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from the west monitor well transect was 5.6 mg/L in the upgradient sand and 3.8 mg/L in the ZVI; the concentration in the ZVI was not much different than the 4.8 mg/L measured in the downgradient sand sample (Figure 5). By November 2003, the Mo concentration in the ZVI sample (7.6 mg/L) was higher than in the upgradient sand sample (3.6 mg/L). The Mo concentration in the downgradient sand sample in November 2003 is similar to that in the ZVI sample suggesting much of the ground water was still flowing through the ZVI zone. By October 2004, the concentration of Mo in the downgradient sand sample (3.8 mg/L) was similar to that in the upgradient sand sample (3.0 mg/L) and vastly different from that in the ZVI sample (20.2 mg/L), indicating that ground water was bypassing the ZVI zone or flowing through preferential pathways without being treated. The increase in Mo concentration in the ZVI is related to an increase in pH value.
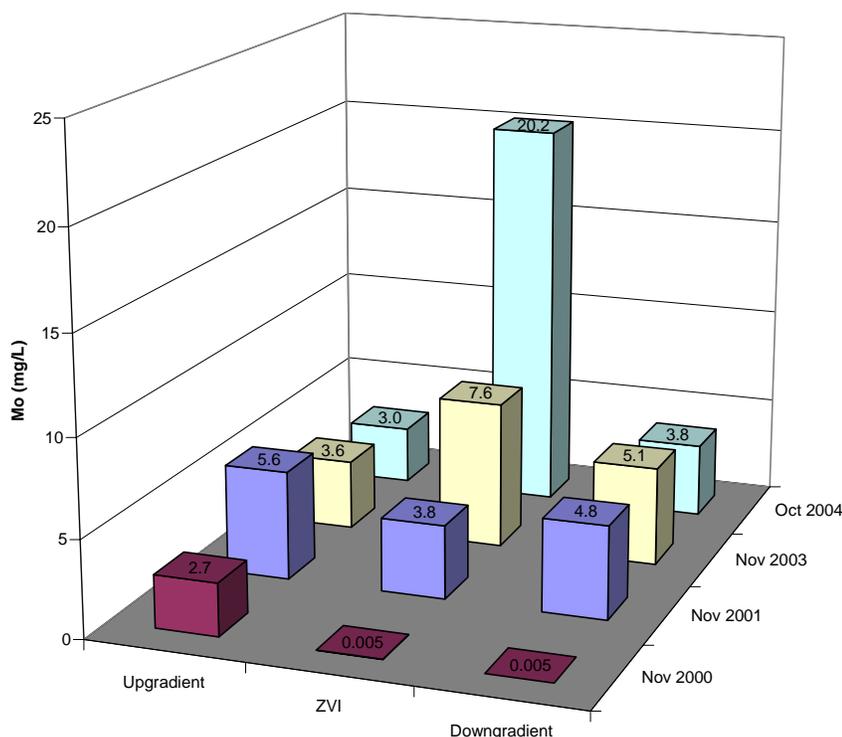
Figure 5. Dissolved Mo concentrations in ground water samples from the upgradient sand, the ZVI, and the downgradient sand from November 2000 to October 2004: west monitoring well transect.

Dissolved U concentrations also indicate a trend from flow through to bypass of the ZVI zone (Figure 6). In November 2001, the U concentration was reduced from 0.92 mg/L in the ground-water sample from the upgradient sand to 0.0006 mg/L in the ground-water sample from the ZVI zone (Figure 6). The concentration in the ground-water sample from the downgradient sand (0.0006 mg/L) reflects concentrations in ground water samples from the ZVI zone, indicating that it is receiving ground water from the ZVI zone. In November 2003, the U concentration in the sample from the downgradient sand (0.29 mg/L) is more similar to samples from the upgradient sand (0.70 mg/L) than to samples from the ZVI zone (0.0004 mg/L), indicating that some ground water is bypassing the ZVI zone. The bypass is even more pronounced by October 2004.

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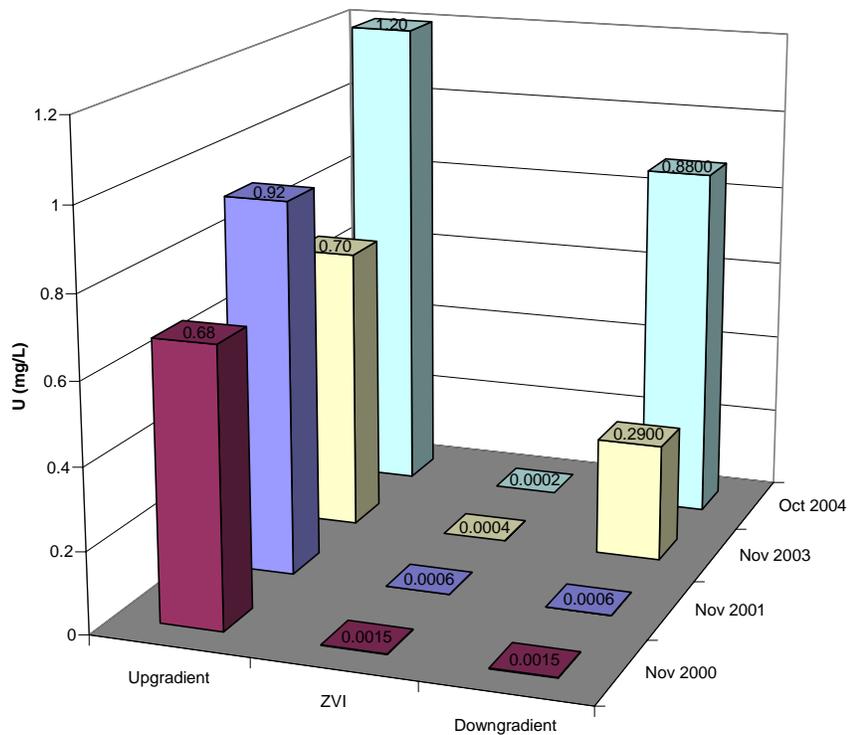
Figure 6. Dissolved U concentrations in ground water samples from the upgradient sand, the ZVI, and the downgradient sand from November 2000 to October 2004: west monitor well transect.

Because Ca and sulfate are also removed from ground water by reaction with ZVI, their concentrations can also be used as ground-water tracers. Calcium and sulfate concentrations confirm the trend from flow through to bypass of the ZVI zone (Figures 7 and 8). Chemical tracer concentration in samples from the other two monitor well transects (central and east) indicate similar trends.

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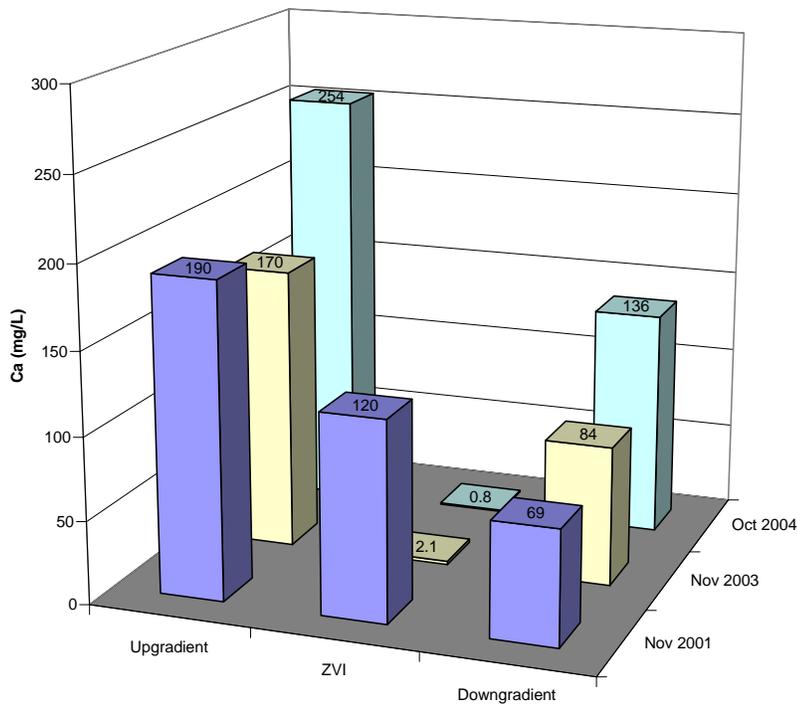
Figure 7. Dissolved Ca concentrations in ground water samples from the upgradient sand, the ZVI, and the downgradient sand from November 2001 to October 2004: west monitor well transect.
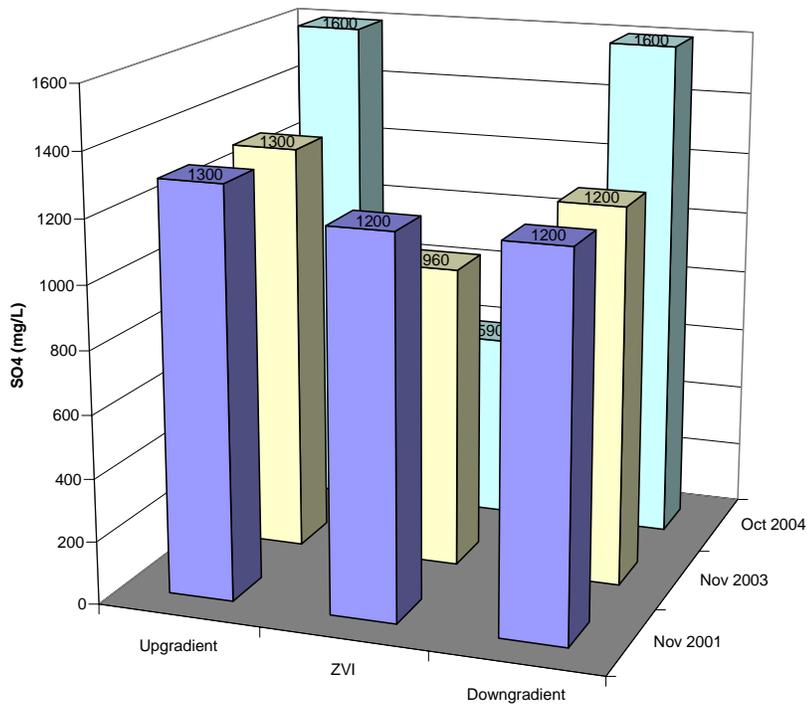
Figure 8. Dissolved sulfate concentrations in ground water samples from the upgradient sand, the ZVI, and the downgradient sand from November 2001 to October 2004: west monitor well transect

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Mounding of the ground-water table in the upgradient sand was coincident with the evolving ground-water chemistry previously discussed. No mounding was observed through 2000 (Figure 9). Mounding began in the first quarter of 2001. Maximum mounding of about 4 ft was achieved by January 2003 and continued until pump back began in early 2004. Mounding was reduced to about 2 ft by the pump back system.
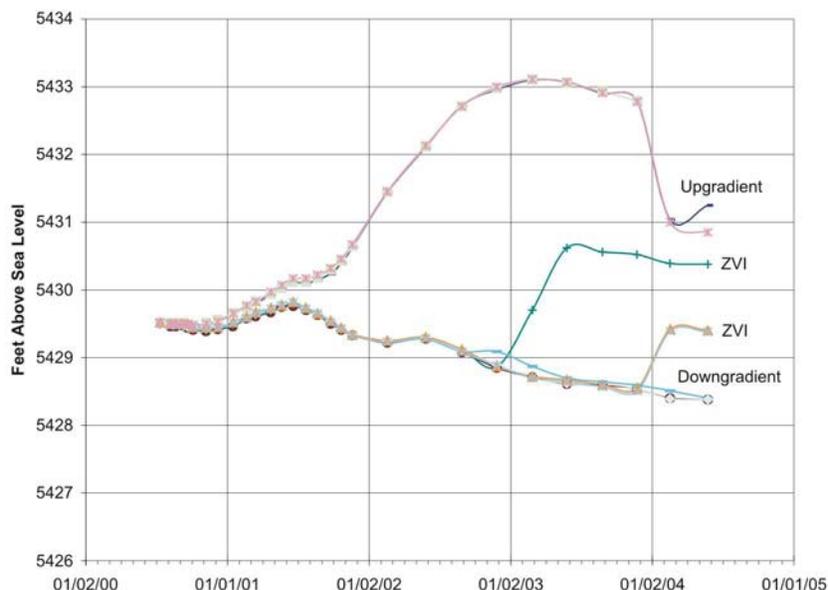
Figure 9. Ground-water elevations in the PRB (Niesen 2000b).

5.0 Performance Assessment Study of the Cotter PRB: Results and Discussion

5.1 Visual Inspection and Sampling of the Cotter PRB

In October 2004, an investigation was initiated to explore the causes of the increasing Mo concentrations and the mounding of ground water. The west end of the PRB was exposed in an excavation to provide direct observation of the ZVI. Figure 10 depicts the excavation after removing overburden. The top of the west concrete side wall and the westernmost line of three monitor wells and three piezometers are exposed (foreground). A 6-ft wide trench was excavated through ZVI in the area of the three wells and the three piezometers; the wells and piezometers were removed as the excavation progressed. The ZVI zone and the two sand zones were exposed to the base of the PRB in the trench. The excavation provided direct observation and sampling of the PRB. Ground water was pumped from the excavation during the investigation. The bottom 2 ft of the excavation immediately above the bedrock was saturated, and a small amount of ground water continued to flow into the excavation from the upgradient sand during the investigation. Prior to and during the excavation, ground water was pumped from a well in the upgradient sand.

The ZVI was excavated in 1-ft lifts, starting with the top lift (7 ft above the base). Samples were numbered with the height (in feet) above the base and distance from the front (upgradient face) of the ZVI zone; thus, cot-2.0-1.0 was collected 2 ft above the base and 1 ft from the front of the ZVI zone.

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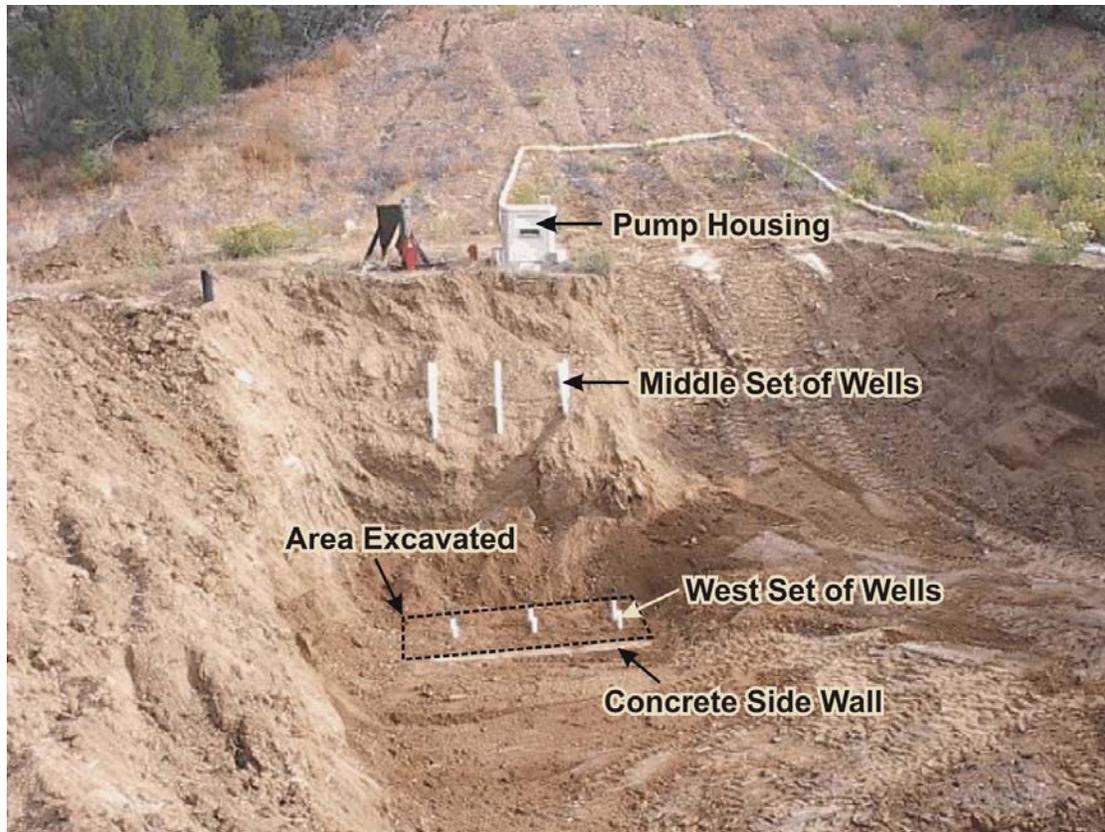
Figure 10. PRB excavated to top of west concrete side wall.

Figure 11 depicts the ZVI zone and the upgradient sand zone beneath the overburden soils. Both sand zones were unaltered and appeared much the same as when they were installed. The ZVI had cemented considerably since installation. Attempts to break the ZVI by impact with the tines of a backhoe bucket were unsuccessful. A mechanical hammer (hydraulically operated), mounted on the backhoe, was required to break apart the ZVI. In the upper 4 ft, a softer zone was observed in the midportion where ZVI was partially friable. ZVI within 2 ft of the upgradient face and within 2 ft of the downgradient face was cemented, whereas the midportion was sufficiently friable to be scooped with a shovel. Except for the uppermost 1 to 2 in. that contained yellow-orange ferric oxide minerals, the ZVI was dark colored. About 0.5 in. of ZVI at the upgradient face also had variable yellow-orange color in the upper 3 to 4 ft.

The cementation of the ZVI indicated the presence of mineral precipitants. Field tests were conducted with dilute HCl; most specimens effervesced, indicating the presence of calcium carbonate minerals. The addition of HCl also caused many of the samples to emit a strong odor of hydrogen sulfide, suggesting the presence of sulfide mineralization. Examination with a binocular microscope in the field revealed the widespread occurrence of translucent crystals believed to be calcium carbonate.
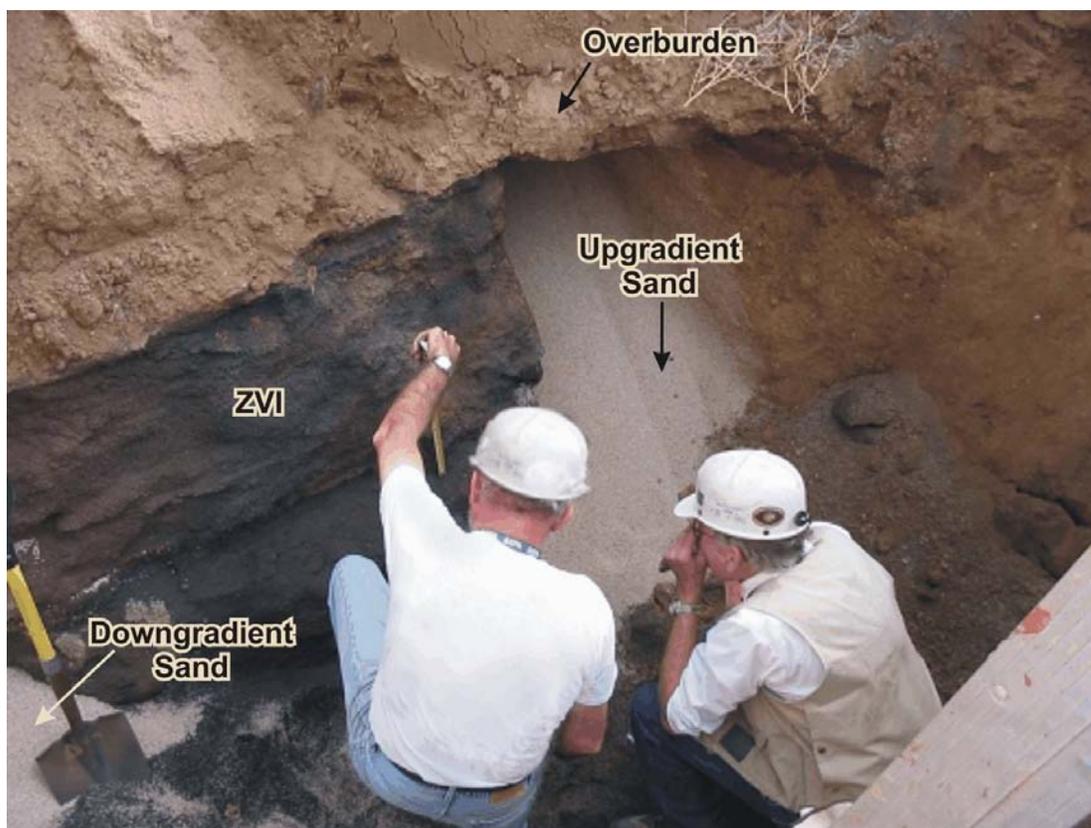
Figure 11. PRB excavation (looking east) showing rigidity of ZVI and the flowing sand of the upgradient sand zone.

5.2 Bulk Chemical Analysis of the Reactive Media

To further define the distribution of mineralization, 24 samples from the ZVI zone were analyzed for bulk chemistry; 12 duplicates from the ZVI zone and 1 sample from the upgradient sand zone were also analyzed. The samples were digested in concentrated nitric acid for 25 min in a microwave oven at temperatures to 180 $^{\circ}$C [procedure SE(MD-1), Stoller 2004]. This procedure has been shown to dissolve more than 95% of the samples and extract all the contamination (Morrison et al. 2003). Uranium in the extracts was analyzed by kinetic phosphorescence [procedure AP(U-2), Stoller 2004], Ca was analyzed by flame atomic absorption [procedure AP(Ca-1, Stoller 2004], and Mo by inductively coupled plasma emission (Paragon Laboratories, Fort Collins, Colorado).

Concentrations of solid-phase U range from less than 5 to 3,727 µg/g, and nearly all the U is within 0.5 ft of the front face of the ZVI (Figure 12). Within 0.5 ft of the upgradient front, U concentrations are high from the base of the ZVI to the 5-ft level and are low in the 6- and 7-ft levels, suggesting that the ground-water table reached a maximum height of about 5 ft. The relatively low U concentration in the 3-ft level indicates that the distribution is heterogeneous. Concentrations of solid-phase Mo range from less than 130 to 4,050 µg/g (Figure 13). Molybdenum concentrations are highest within 0.5 ft of the upgradient face of the PRB, but Mo concentrations are more elevated than U concentration in samples collected farther into the PRB, particularly in the 1- and 2-ft levels.

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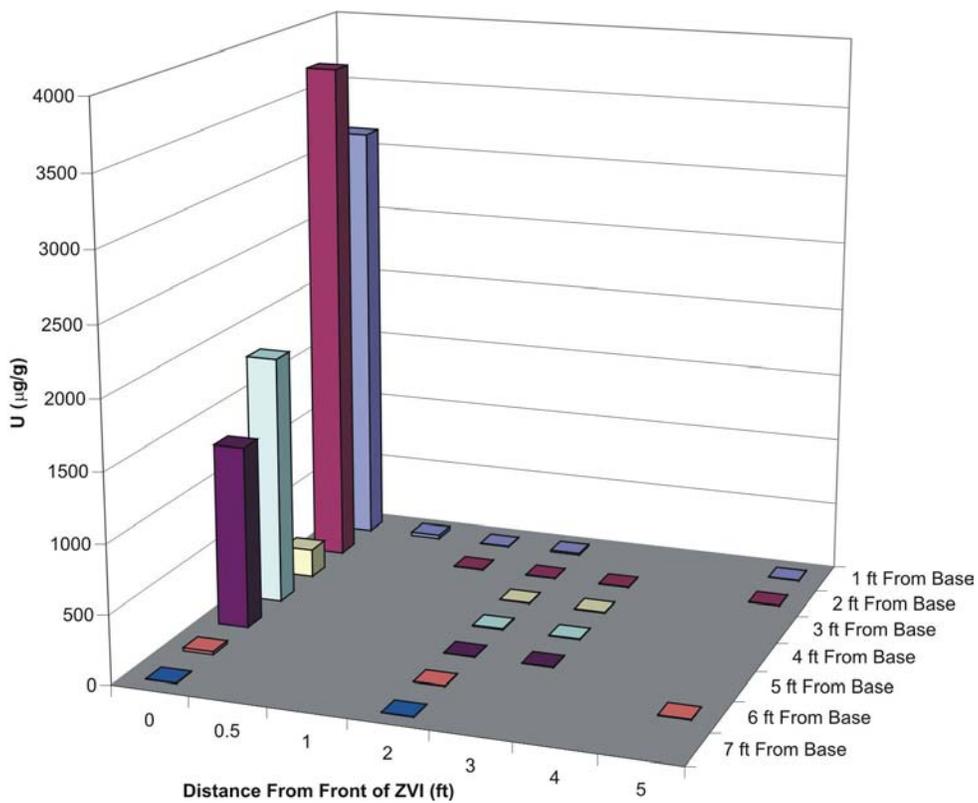
Figure 12. Distribution of solid-phase U in PRB.
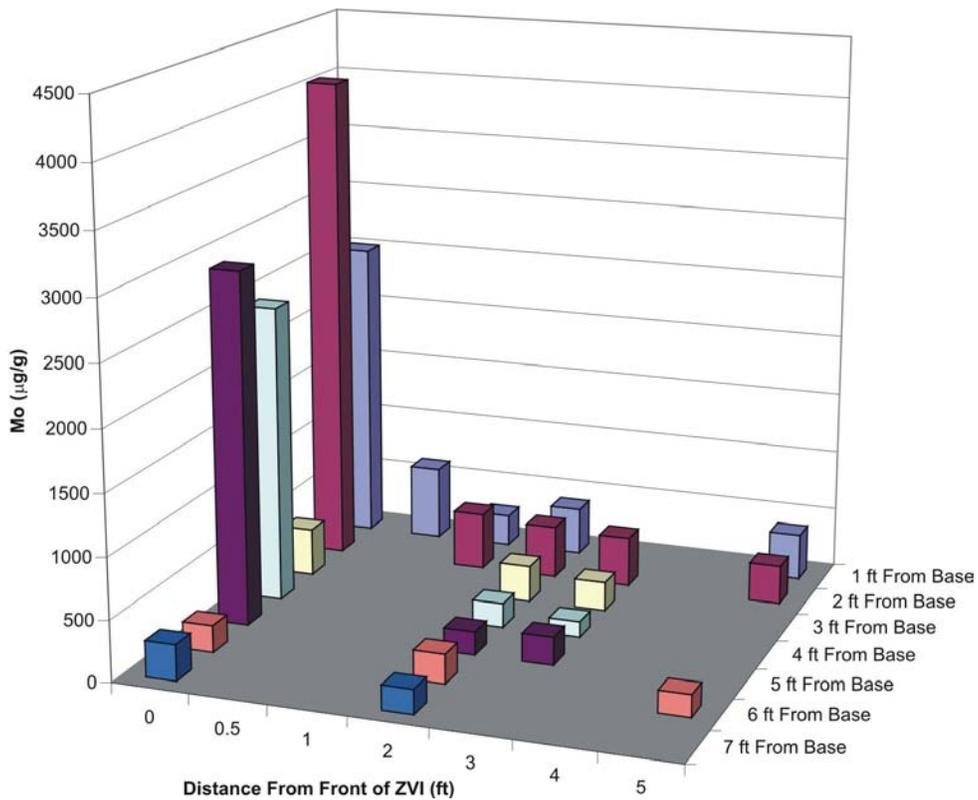
Figure 13. Distribution of solid-phase Mo in PRB.

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Similar to the distributions of U and Mo, concentrations of Ca are high in the zone within 0.5 ft of the upgradient face (Figure 14). However, Ca is also present in high concentrations throughout most of the ZVI zone in the 1- through 3-ft levels. Calcium concentrations range from less than 0.5 to 44,200 µg/g. Calcium carbonate minerals cementing ZVI is likely one of the causes of the rigidity of the ZVI and is also a significant factor in the loss of hydraulic conductivity, indicated by the mounding of the ground-water table in the upgradient sands and alluvium.
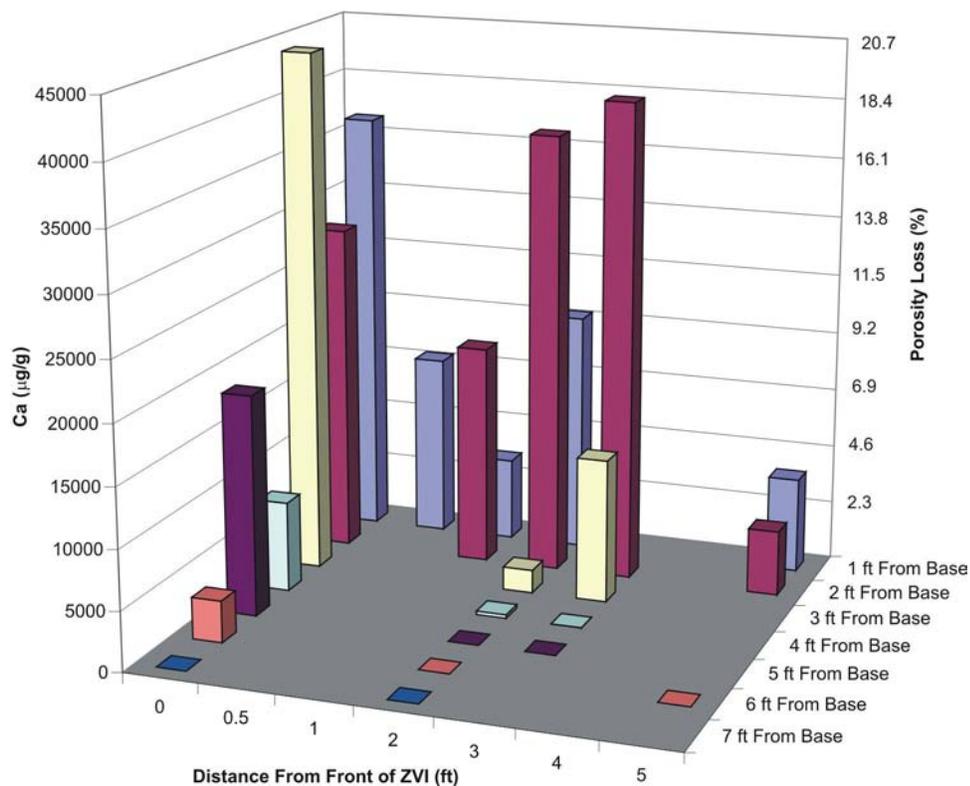
Figure 14. Distribution of solid-phase Ca in the PRB.

Assuming that all Ca resides in the mineral calcite (a type of calcium carbonate), the amount of porosity in the saturated portion of the ZVI lost because of calcium carbonate precipitation can be calculated. An independent estimate of the porosity loss can be made using the chemical gradients based on ground-water chemistry and an estimated ground-water flux. The predictions of porosity loss based on bulk solid-phase chemistry and ground-water gradient data are 9.4% and 18.3%, respectively (Table 2). If, by February 2002, the ground-water flux is assumed to have decreased to nearly zero due to bypass, the estimate of porosity loss based on ground-water gradient is 9.5% rather than 18.3% and is much closer to that based on bulk chemistry (Table 2). Similar predictions of porosity loss because of sulfide mineral precipitation are 6.1% and 1.4% (Table 2). Together with ferric oxide precipitation, which cannot be estimated reliably, the loss of porosity is substantial and could account for significant decreases in hydraulic conductivity. If more of the precipitation occurred in a confined zone (such as the front 0.5 ft), the effect on ground-water flow would be even more severe.

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The bulk chemistry distributions observed in the Cotter PRB are consistent with those observed in a ZVI-based PRB at Monticello, Utah (Morrison 2003). In the Monticello PRB, U is concentrated at the upgradient portion of the PRB, and Ca is distributed throughout the PRB. The maximum concentration of Ca in the Monticello PRB is about 47,000 μg/g, which is similar to the Cotter site. However, U concentrations at Monticello were as high as 800,000 μg/g, which are considerably higher than the U concentrations observed at the Cotter site. Molybdenum was not analyzed in the Monticello study.

Table 2. Estimates of porosity loss because of mineral precipitation based on bulk chemical analysis of solids and from ground-water chemical gradients.

Mineral Phase	Bulk Chemistry	Ground Water Gradient (by October 2004)	Ground Water Gradient (by February 2002)
CaCO$_3$	9.4%	18.3%	9.5%
Ferrous sulfide (FeS)	not analyzed	6.1%	1.4%
Total CaCO$_3$ and FeS		24.4%	10.9%

5.3 Measurement of Hydraulic Conductivity

Hydraulic conductivity measurements were made on 3 samples of the ZVI zone using flexible wall permeameter. The samples were cast in concrete and two-in.-diameter while they were cored with a 2-in.-diameter cement drill. Hydraulic conductivity was measured on the cores while under confining pressure.

The three samples were collected 7-ft from the base of the ZVI and 2.5 ft from the front face (7.0-2.5), 2.0 ft from the base and 2.5 ft from the front face (2.0-2.5), and 1.0 ft from the base and 0.5 ft from the front face (1.0-0.5). Hydraulic conductivities measured on samples 7.0-2.5, 2.0-2.5, and 1.0-0.5 were 2.1×10^{-4}, 1.3×10^{-3}, and 5.0×10^{-4} cm/s, respectively. These measurements indicate that the hydraulic conductivity of the ZVI decreased by about 1 to 2 orders of magnitude.

The higher hydraulic conductivity measured on sample 2.0-2.5 (1.3×10^{-3} cm/s) is consistent with visual observations of friable material in the mid portion of the ZVI. All three measured hydraulic conductivities are considerably less than the hydraulic conductivity of the original ZVI, estimated to have been about 7×10^{-2} cm/s. Within the lower 2 ft of the ZVI, the hydraulic conductivity near the front face (5.0×10^{-4} cm/s) is less than that in the midportion, suggesting more plugging near the front face. Sample 7.0-2.5 was collected within 2 in. of the top of the ZVI where it has oxidized, probably from contact with overlying unsaturated sediments. The low conductivity in this sample is likely due to the accumulation of hydrous ferric oxides. The hydraulic conductivities measured on these three samples are similar to the hydraulic conductivities measured on ZVI at the Monticello site by using gas-injection slug tests (DOE 2005).

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5.4 Observations of Reactive Media Using Petrographic, Scanning Electron Microscope, and Electron Microprobe Methods

Samples of the ZVI were observed with a binocular microscope, reflected light petrographic microscope, scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDX), and an electron microprobe (EM). Samples were dried under vacuum within two weeks of sample collection. Dried samples were viewed without additional preparation under a binocular microscope. Samples for SEM investigations were glued to aluminum stubs and coated with carbon. Samples for use with the petrographic microscope and the EM were set in 1-in.-diameter mounts with epoxy. No water was used when the epoxied plugs were cut with a diamond saw. The cut surface was again coated with epoxy to ensure that all pore spaces were filled. The surface was then polished to a mirror finish using aluminum carbide polishing compounds.

Observations with the binocular microscope revealed ubiquitous translucent crystals of calcium carbonate. Bladed crystal habits suggest aragonite rather than calcite. Figure 15 depicts several ZVI grains with mats of calcium carbonate crystals on their surfaces. Figure 16 depicts calcium carbonate crystal coatings that precipitated along ZVI grain boundaries and are cementing the grains together. Figure 17 shows another ZVI surface that is nearly covered with bladed calcium carbonate crystals. These types of calcium carbonate crystals are ubiquitous in most ZVI samples from the lower 4 ft of ZVI in the PRB.
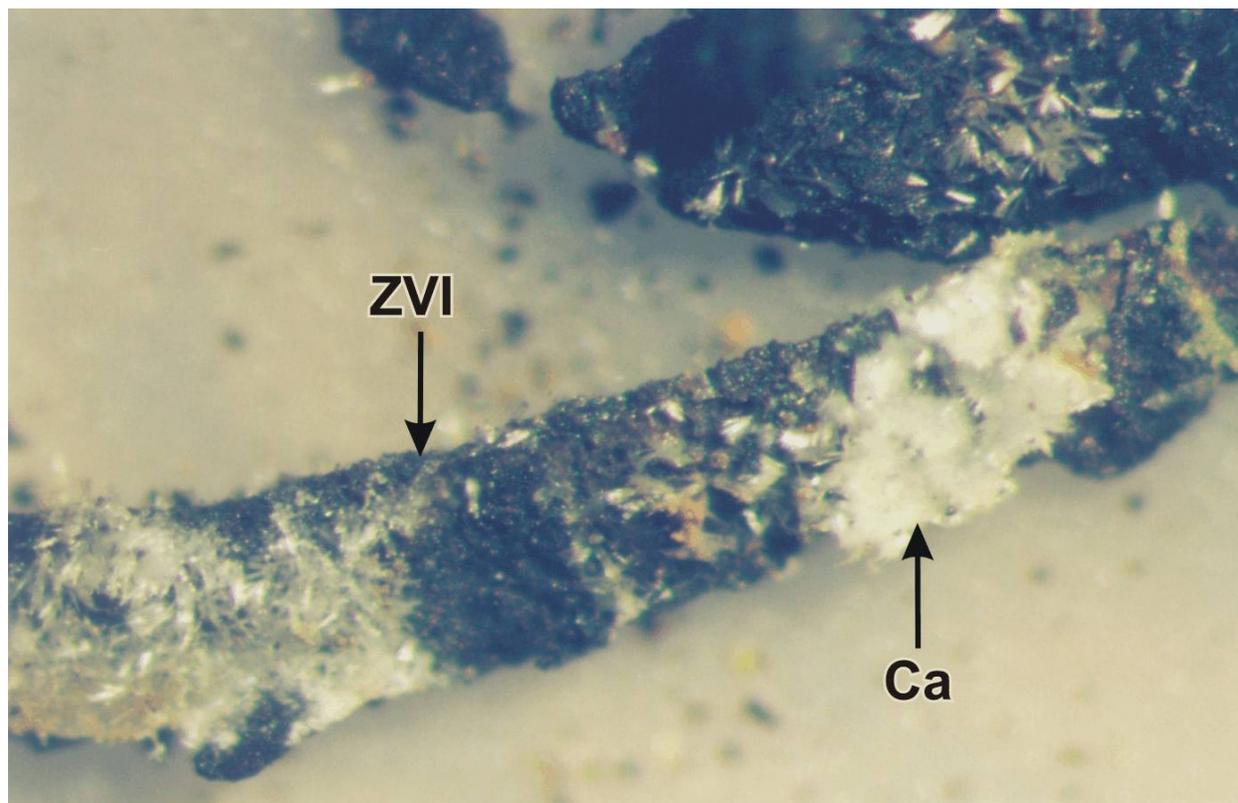
Figure 15. Photomicrograph of ZVI grain with mats of calcium carbonate crystals (Ca). Sampled October 28, 2004, 1 ft above base of ZVI and 1 ft from upgradient face of ZVI. Width of photo 2.5 mm.

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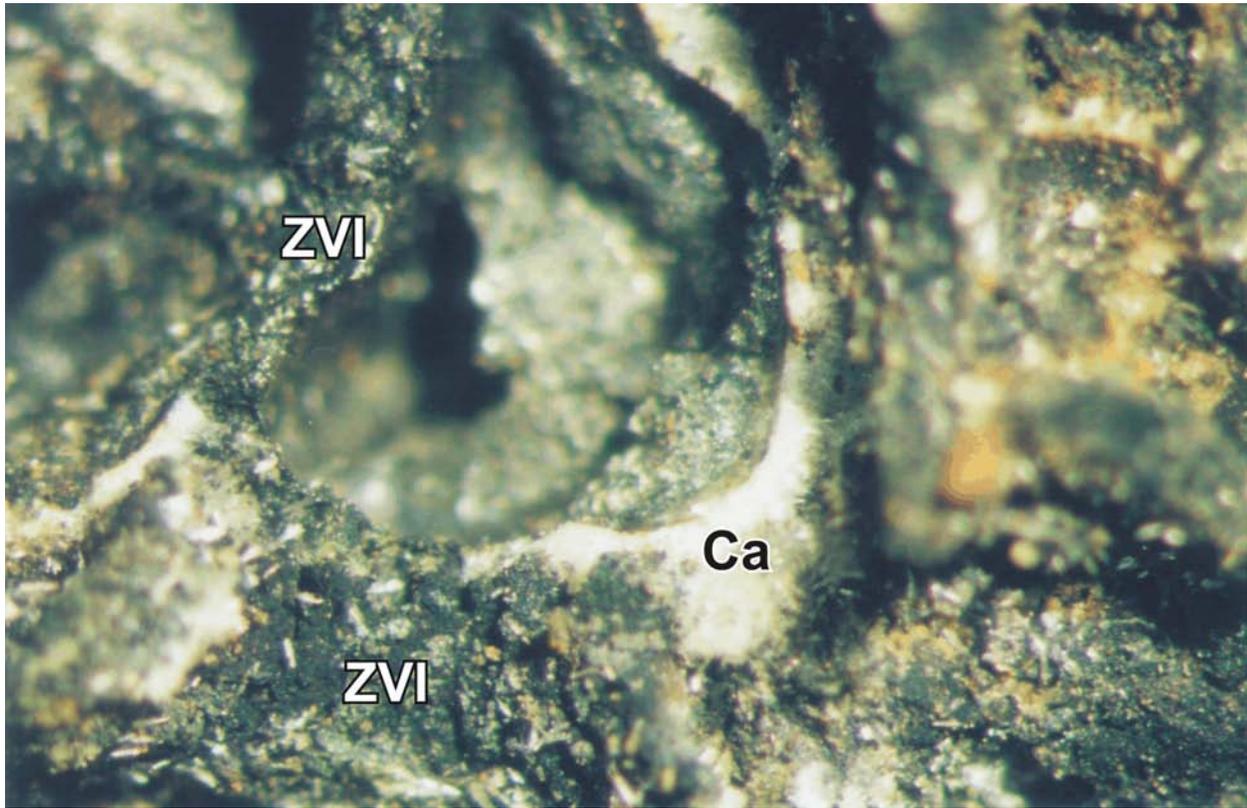
Figure 16. Photomicrograph of calcium carbonate crystals (Ca) coating grains of ZVI. Sampled October 28, 2004, 1 ft above base of ZVI and 1 ft from upgradient face of ZVI. Width of photo 4 mm.

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Figure 17. Photomicrograph image of bladed calcium carbonate crystals nearly completely coating the surface of a ZVI grain. Sampled October 28, 2004, 1 ft above base of ZVI and 0.5 ft from upgradient face of ZVI. Width of photo 2 mm.

Figures 18 and 19 are SEM photomicrographs images of bladed crystals of calcium carbonate growing on iron oxide coatings of ZVI grains; the calcium carbonate is partly or totally filling the pore space. EDX analyses of Ca and Fe were used to confirm the identification of calcium carbonate and iron oxide minerals. EDX analysis also detected sulfur in the iron oxide coatings.

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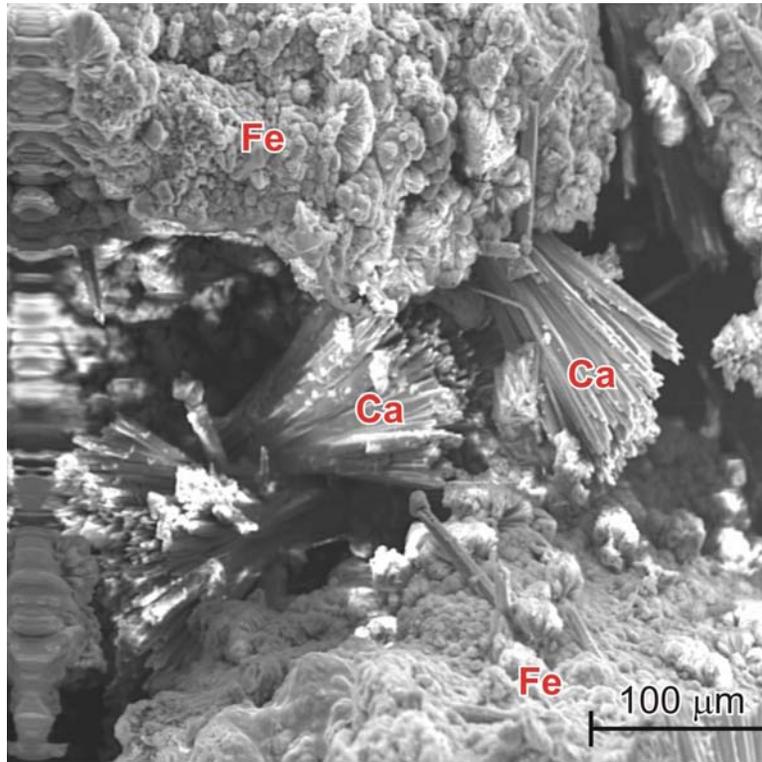
Figure 18. SEM photomicrograph image of bladed calcium carbonate crystals (Ca) partially filling pore spaces among iron oxide (Fe) corrosion products.
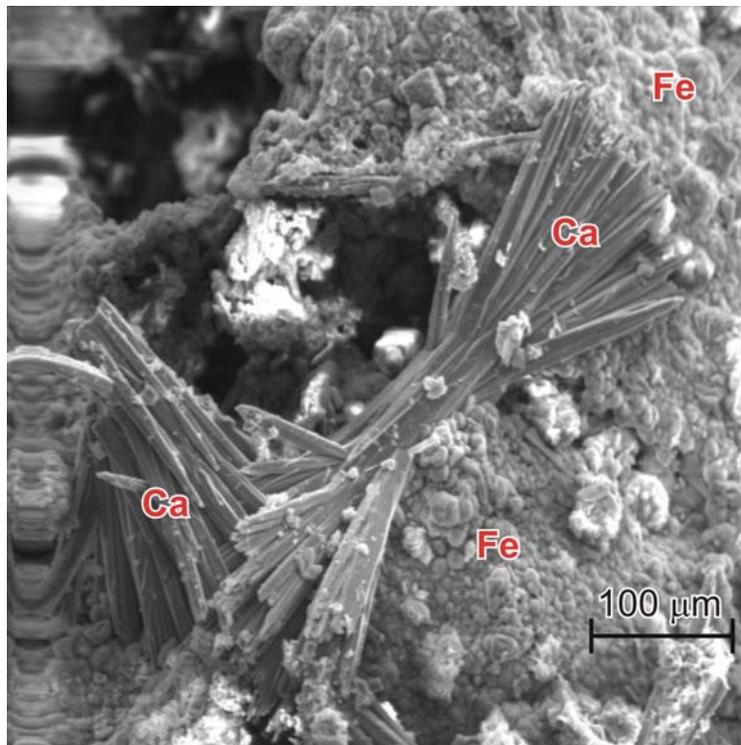
Figure 19. SEM photomicrograph image of bladed calcium carbonate crystals (Ca) precipitated on iron oxide (Fe) corrosion products.

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EM methods allow a more accurate and comprehensive analysis of the chemical compositions. The electron beam used for the EM investigation was about 10 μm; analyses of crystals that are smaller than 10 μm will be influenced by x-rays emanating from surrounding crystals and by absorption by micrometer-sized voids. Because EM can provide a complete chemical analysis of the electron beam's interrogated area, minerals can often be identified based on chemical stoichiometry.

An EM photomicrograph of fresh Peerless ZVI grains is presented in Figure 20. ZVI grains appear as bright, well-polished surfaces. This cast iron product typically contains a variety of graphite inclusions and has a silica content of about 2 to 3% (all percentages are in weight-percent). No oxidation products are associated with the fresh ZVI sample.
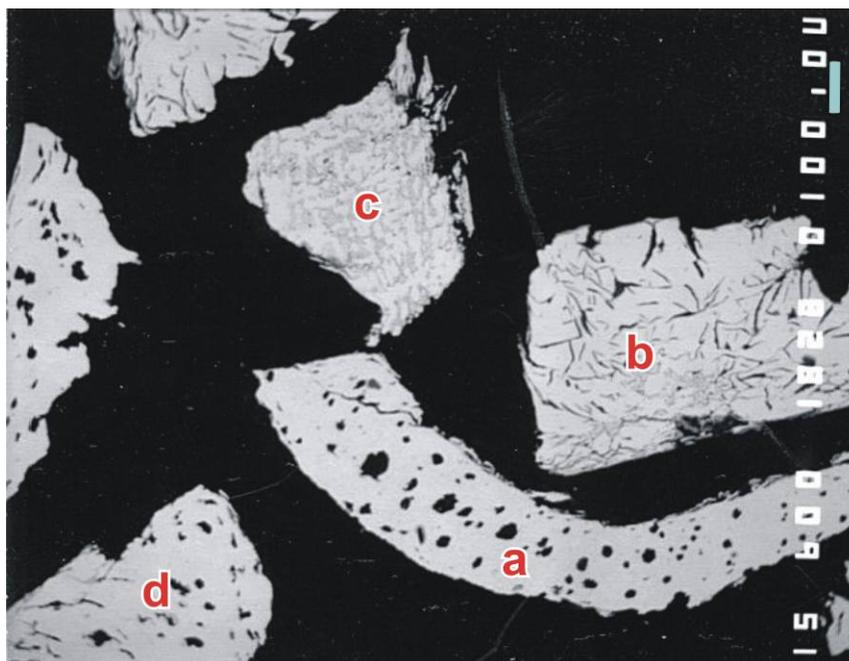
Location	Weight–%	
	Fe	Si
a	97.0	2.6
b	97.2	2.2
c	97.4	2.1
d	98.2	2.5

Figure 20. Fresh unaltered Peerless ZVI grains containing graphite inclusions. No corrosion products are present. Letters refer to chemical analyses. Blue bar in upper right is 100 μm long.

Calcium carbonate crystals and ZVI grains are large and well polished, providing sufficient surface for accurate EM analysis that total nearly 100%. Although carbon was not analyzed, the stoichiometry of Ca is nearly perfect for $CaCO_3$. EM analysis of alteration products, other than calcium carbonate, were often imperfect because of low analytical totals caused by (1) oxygen and carbon not being analyzed; (2) crystals that are smaller than the electron beam

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(approximately 10 μm), resulting in a combined analysis of many different crystals; (3) submicron crystals that are not perfectly flat, lowering the intensity of the signals;, and (4) submicron pores that reduce the signal. Despite these limitations, the EM analyses provide important information on element associations, minimum analytical concentrations, and in many cases, sufficiently complete data to positively identify a mineral or mineral group.

Figures 21 through 25 are EM photomicrographs of the zone 1 ft above the base of the ZVI and 0 to 0.5 ft from the front, where most of the U and Mo is concentrated. Figure 21 shows a large ZVI grain and several smaller blade-like grains. The black area is a void between alteration rims. Calcium carbonate appears as well-polished, dark areas (some are labeled Ca). Thick (20 to 100 μm) alteration rims containing calcium carbonate, iron oxide, and iron sulfide surround the void. Iron sulfide mineralization, seen as a thin bright rim, is apparently a late-stage overprint. Sulfur concentrations are as high as 20% and are always present as sulfide (as determined by the spectral shift). Molybdenum concentrations up to 0.57% occur in the sulfidic alteration rims.

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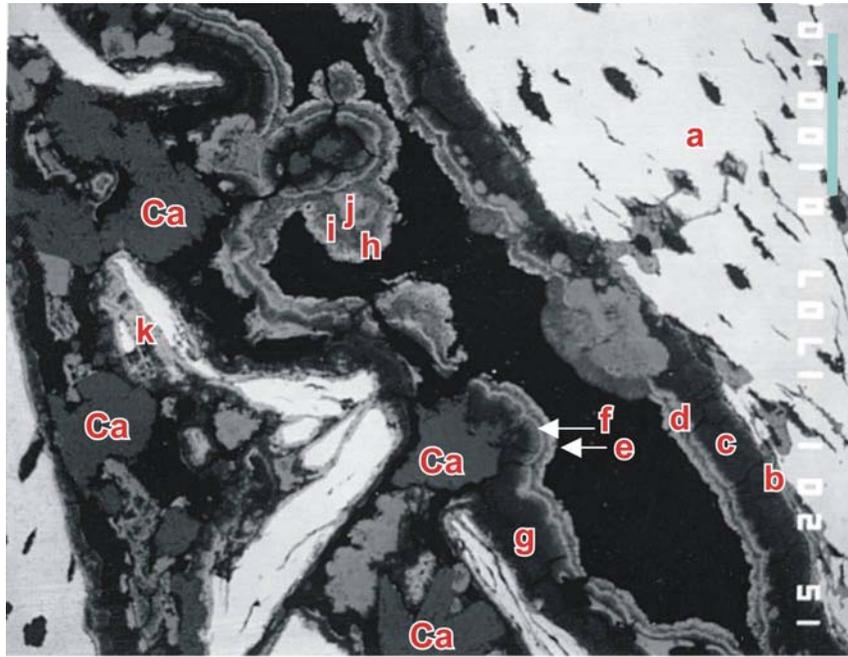
Location	Weight-%				Description
	Mo	Fe	S	Si	
a		96		2.3	ZVI
b	0.57	61	0.47	1.4	
c	0.24	21	3.9	2.6	
d		60	19	0.3	Iron Sulfide Rim
e		60	19	0.04	Iron Sulfide Rim
f	0.15	50	2.8	0.9	Iron Oxide (hydrate)
g	0.19	24	4.5	1.6	
h		59	20	0.04	Fe Sulfide Rim
i		41	14	0.1	
j		49	14		
k		68		2.3	
Ca					CaCO$_3$

Figure 21. ZVI 1.0 ft from base, 0.5 ft from front. This image shows ZVI grains and a thick altered zone containing calcium carbonate, iron oxide, and iron sulfide. Letters refer to chemical analyses. Blue bar in upper right is 100 µm long.

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Figure 22 shows another area of the sample collected 0.5 ft from the front. Several ZVI grains are coated with corrosion products. Grains of iron carbonate or carbonate-hydroxide (a, b, and c) are cemented by iron sulfide (d, e, and f). It appears that the sulfidic cementation occurred after the formation of the iron carbonate grains. Molybdenum concentrations up to 0.25% are associated with the iron carbonate, whereas the sulfide is devoid of Mo.
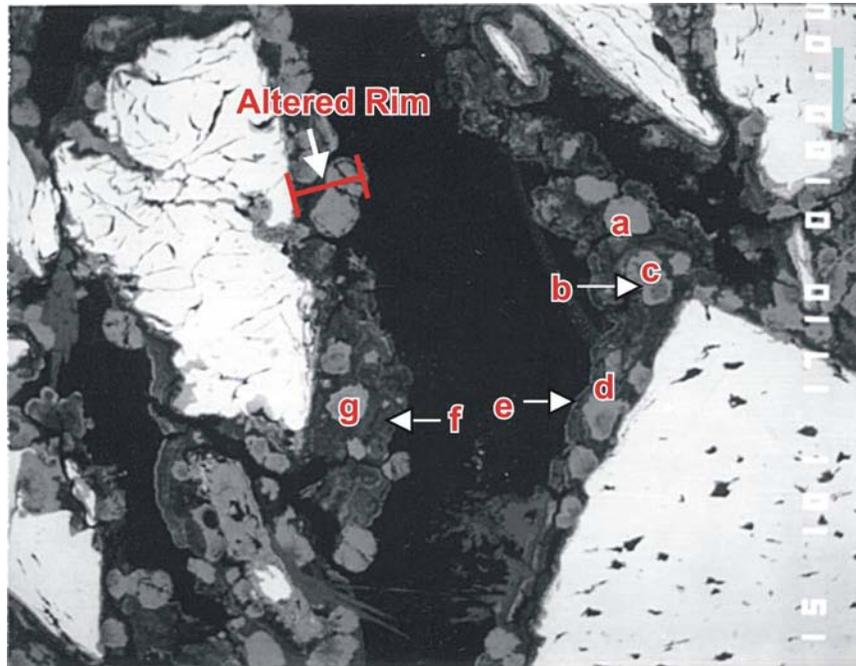
Location	Weight-%			
	Mo	Fe	S	Si
a	<0.05	57	<0.05	
b	0.06	53	0.1	
c	0.24	53	0.2	0.9
d		33	12	0.8
e	<0.05	42	14	
f	<0.05	39	14	1.2
g	0.25	55	0.12	

Figure 22. ZVI 1.0 ft from base and 0.5 ft from front. Shows ZVI grains and thick altered rims containing iron oxide and iron sulfide. Letters refer to chemical analyses. Blue bar in upper right is 100 µm long.

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Figure 23 shows an area of a sample collected within 1 in. of the front in the ZVI zone. Iron oxide forms a pseudomorph ("a" on photomicrograph) of a large ZVI grain. Pseudomorphic replacement preserves the grain shape and volume but replaces the ZVI with iron oxide. Because volume is preserved and Fe concentration decreases, some Fe is released during this type of alteration. The pseudomorph has a Mo concentration of 0.48% but no U is present. Calcium carbonate (probably aragonite) is present as large (up to 200-μm-thick) crystals, projecting into and partially filling voids (some are labeled Ca). Iron sulfide occurs as white spots within the calcium carbonate (d) and thin bright rims (e and f) over the calcium carbonate; with sulfur concentrations up to 29%. Molybdenum concentrations to 6.5% and U to 1% are associated with the sulfidic alteration. These concentrations of Mo are too high to be adsorbed and indicate the presence of Mo-bearing minerals.
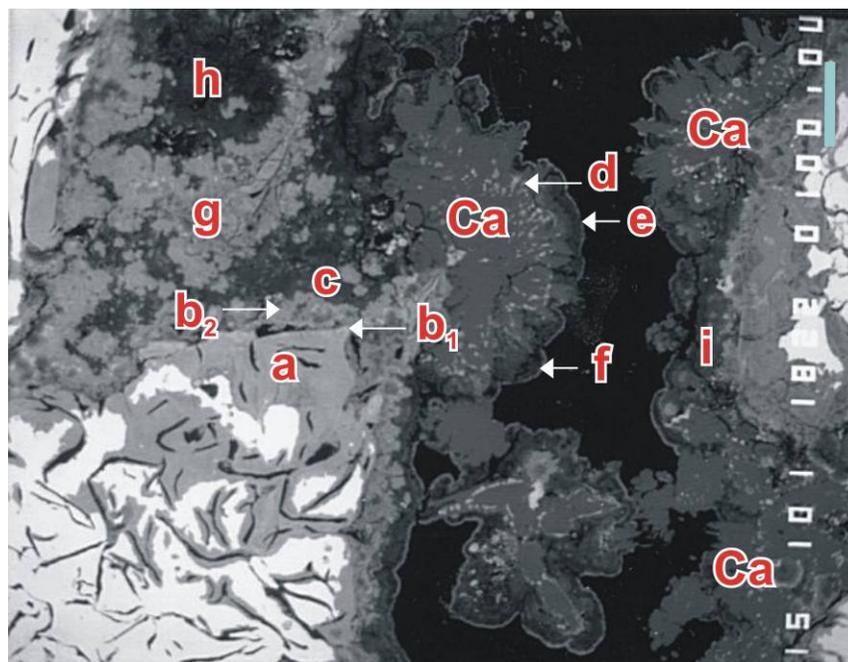
Location	Weight-%						Description
	Ca	U	Mo	Fe	S	Si	
a			0.48	64	0.6	4.2	Probably iron oxide (hydrate)
b_1	1.1	1.0	6.4	52	6	4.8	Slightly lighter edge
b_2	1.4	0.27	6.5	58	6	3.4	
c	0.14	<0.05	1.1	32	13	1.0	
d	1.5	0.07	0.43	56	29	1.6	White spots
e	0.16	0.07	0.35	41	8	2.8	Darker zone
f			0.12	50	12	0.6	Lighter rim
g	0.79	0.07	6.3	58	8	1.7	Lighter material
h	0.1		1.0	27	12	0.8	
i	0.2	0.12	0.72	33	14	1.0	
Ca							CaCO_3

Figure 23. ZVI 1.0 ft from base and 1 in. from front. Shows ZVI grains with pseudomorphic replacement by iron oxide, thick altered rims containing calcium carbonate, iron oxide, and iron sulfide. Letters refer to chemical analyses. Blue bar in upper right is 100 μm long.

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Figure 24 (A) shows another area of a sample collected 1 ft above the base of the ZVI and within 1 in. of the front. Iron oxide pseudomorphs have replaced more than 50% of several ZVI grains. The pseudomorphs contain up to 0.5% Mo but no U. Corrosion products, consisting mostly of iron sulfide with a small amount of iron oxide, fill most of the pore spaces among the ZVI grains. Uranium concentrations to 31% occur in thin bright, sulfide-bearing zones coating other corrosion products. Uranium concentrations of this magnitude indicate that discrete U minerals are present. As indicated by element distribution maps, U and sulfur are spread throughout the alteration coatings (B and C). Uranium is also present in lesser but significant concentrations (to 2.7%) in darker areas containing sulfidic corrosion products. Molybdenum concentration to 5.6% are present in some of these same sulfur-bearing areas. Areas low in sulfur are also typically low in Mo and U. Calcium is confined to a few discrete grains of calcium carbonate (D).
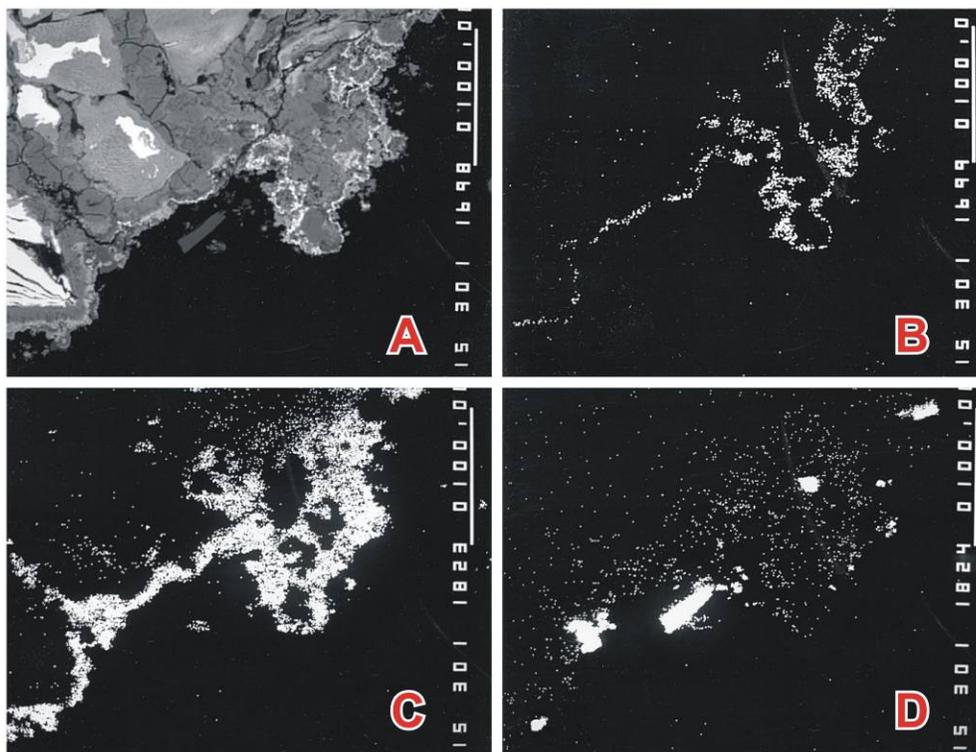
Figure 24. ZVI 1.0 ft from base and within 1 in. of front. *(A) ZVI grains with large pseudomorphic replacements by iron oxide. Pseudomorphic iron oxide is low in Mo and U. Corrosion products include iron silicate, iron sulfide, iron oxide, and calcium carbonate. (B) U map. (C) sulfur map. (D) Ca map. White bars in upper left of each figure are 100 µm long.*

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Figure 25 is an EM photomicrograph image of a portion of the ZVI at the back side (5.0 ft from the front) and 1.0 ft from the base. Even at this distance from the front there is abundant corrosion of the ZVI, pseudomorphic replacement of ZVI (a), and widespread deposition of iron oxides (b) and possibly iron carbonate (d, f). Sulfide is present but does not seem as abundant as in the samples collected closer to the front. Large calcium carbonate crystals (Ca) occlude pore space and appear to have grown after deposition of most of the other corrosion minerals.

Location	Weight-%				Description
	Ca	Fe	S	Si	
a		64	0.2	3.8	
b	0.03	61	0.4	1.0	
c	0.69	54	1.7	1.5	
d	0.81	39	1.1	1.4	
e	0.52	58	0.2	0.4	
f	0.71	33	1.7	1.1	
g	0.85	57	0.9	1.5	
h	27.6	7.4	0.3	2.6	
i	0.77	52	2.8	1.1	
Ca					$CaCO_3$

Figure 25. ZVI 1.0 ft from base at back of ZVI and 5.0 ft from front. Left: ZVI grains with pseudomorphic replacement by iron oxide (a) and thick altered rims containing mostly (hydrous) iron oxides (b). Large crystals of calcium carbonate (Ca) are adjacent to and overprint the oxide coatings. Right: Distribution of sulfur. Letters refer to chemical analyses. White bars in upper right of each figure are 100 µm long.

5.5 Effect of Acid Treatment: Bench-Scale Observations

Several bench-scale tests were conducted to determine if chemical removal of corrosion minerals is possible. Treatment agents were 10% HCl, Lime Away, and EDTA. Lime Away is a commercial household cleanser distributed by Reckitt Benckiser, Inc., that was developed to remove rust, calcium, and lime. In all cases, the treatments showed positive effects by causing disaggregation of the cemented ZVI matrix and removal of minerals from the ZVI grain surfaces. Results of these investigations are only qualitative, because treatment agent concentrations, ratios of treatment agents to ZVI, and agitation times were not rigidly controlled.

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The HCl appeared to be the most effective treatment agent, based on its ability to disaggregate the sample and on microscopic observations of the mineral grains before and after treatment. Figure 26 (top) shows ZVI coated with mixtures of black oxides and calcium carbonate minerals. Figure 26 (bottom) shows a sample that was treated for about 1 hour in 10% HCl; this sample was a cemented chunk of ZVI prior to treatment. The HCl treatment resulted in complete disaggregation of the ZVI and removed the black carbonate oxide coatings. The ZVI following HCl treatment appears similar in appearance to fresh ZVI. A secondary electron image of the HCl-washed ZVI shows bright areas of clean ZVI and dark stringers of graphite; no corrosion products are present (Figure 27). Although qualitative, these observations suggest that a weak acid may be used to rejuvenate ZVI that has undergone extensive corrosion in a PRB. Uranium and Mo concentrations in the acid were not measured but it is likely that they would be elevated and the fluid would need to be extracted and disposed.

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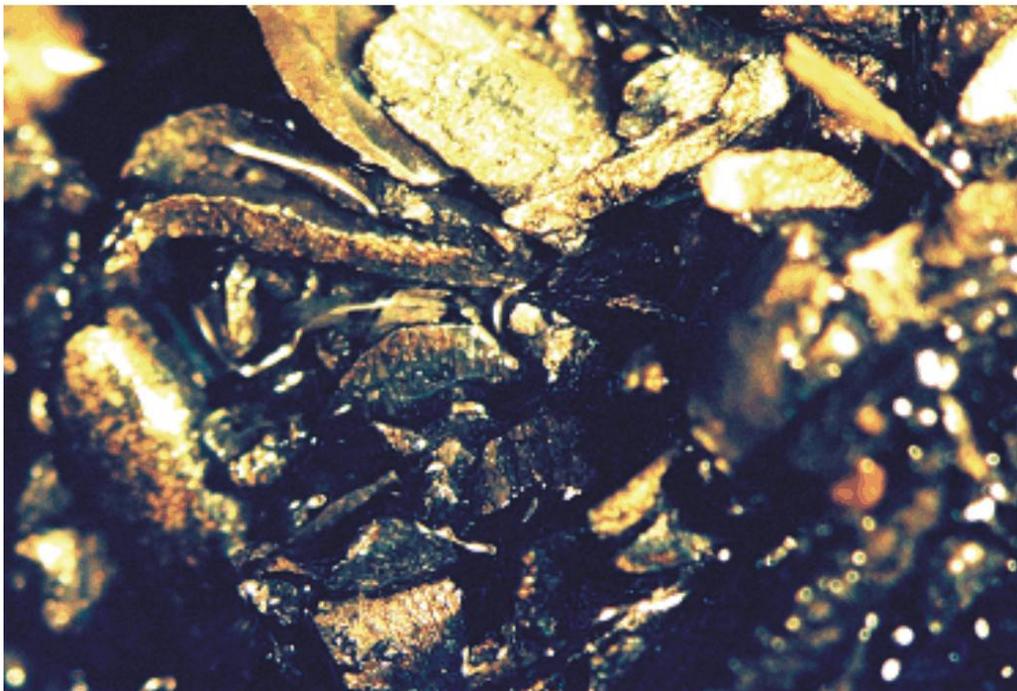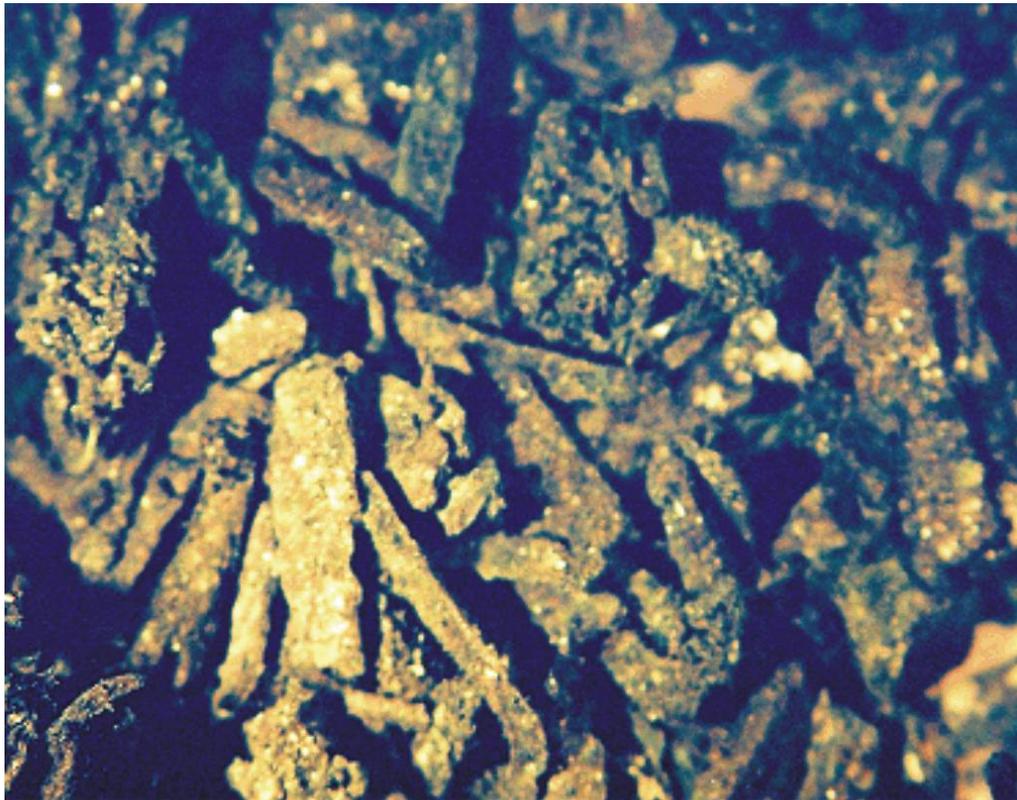
Figure 26. Photomicrographs showing effect of acid washing. Top: ZVI from PRB before HCl treatment, shows black "sooty" coatings. Width of photo is 17 mm. Bottom: ZVI from PRB after washing in 10% HCl shows absence of black "sooty" coatings. Width of photo is 10 mm.

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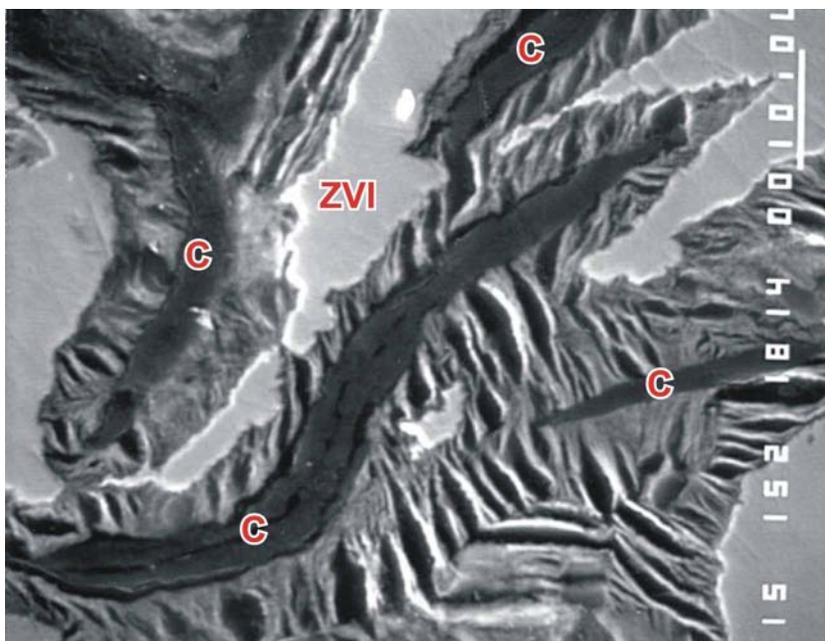
Figure 27. Secondary electron image of the same sample in Figure 26 showing ZVI after washing in 10% HCl. The entire sample looked similar to this. The dark gray stringers are carbon (C), probably graphite.

5.6 Column Test Using Zero-Valent Iron Sampled From the Cotter PRB

A column test was conducted December 6, 2004 through January 20, 2005 to determine if ZVI from the Cotter PRB is still reactive for uptake of Mo. Other test objectives included determining reactivity for U and evaluating mineral precipitation.

The test used ZVI collected on October 27, 2004, 2.3 ft from the base of the ZVI and 2.5 ft from the front face. The sample contained relatively friable ZVI. The ZVI (2082 g wet weight) was packed moist into a 2-in.-diameter and 18-in.-tall clear acrylic column. On the basis of analysis of moisture content, the equivalent dry weight of the ZVI is 1914 g. A synthetic ground water with major ion chemistry similar to that in well 1455 sampled on May 25, 2004, was used as influent for most of the test. This well is immediately upgradient of the PRB and the water is representative of ground water entering the PRB. Table 3 presents a comparison of the composition of the ground-water sample to the synthetic ground water. The small compositional differences are within analytical uncertainty. During one period of the test, a second synthetic ground water was used that simulated ground water collected from well 1453, water with high pH values, from within the ZVI zone (Table 4). Synthetic ground water was pumped through the column from bottom to top with a peristaltic pump.

Dissolved oxygen (DO) concentrations were kept low (generally less than 0.4 mg/L) by constantly purging the 20-L source tank with inert gas (about 0.5 to 1 Lpm). Dissolved oxygen was monitored daily using the diffusion membrane method [procedure AP(DO-1), Stoller 2004]. The pH values were controlled by injecting a small amount of carbon dioxide gas into the inert gas stream bubbling into the source tank. Chemistry of the source tank was monitored daily. Samples were collected using a fraction collector. Effluent samples were immediately acidified

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with 1% concentrated nitric acid to prevent ferric oxides from forming and to preserve the samples prior to analysis. Samples taken and analyzed were clear with no suspended matter. Uranium was analyzed by kinetic phosphorescence [procedure AP(U-2), Stoller 2004], Mo was analyzed colorimetrically by the ternary complex method [procedure AP(Mo-3), Stoller, 2004], sulfate and chloride were measured by ion chromatography [procedures AP(SO_4-4) and AP(Cl-2), Stoller 2004], and Fe and Ca were analyzed by flame atomic absorption [procedures AP(Fe-1) and AP(Ca-1), Stoller 2004]. Alkalinity was determined by titration with sulfuric acid [procedure AP(Alk-1), Stoller 2004]. Oxidation reduction potential (ORP) and pH values were measured in both influent and effluent water with in-line electrodes and were calibrated daily. The ORP and pH value data were recorded at 0.5 min intervals with a datalogger. The experimental apparatus is depicted in Figure 28.

Table 3. Composition of ground water sampled upgradient of the prb and composition of the synthetic ground water (SGW-1455) used in the column test.

Constituent	Ground Water From Well 1455 Sampled May 25, 2004	SGW-1455
Sodium (mg/L)	370.0	371.5
Potassium (mg/L)	4.50	4.49
Calcium (mg/L)	250.0	249.8
Magnesium (mg/L)	87.0	88.79
Sulfate (mg/L)	1400	1208
Chloride (mg/L)	96.0	96.5
Inorganic Carbon (mg/L)	98.0[a]	97.9
Molybdenum (mg/L)	1.9	8.05[b]
Uranium (mg/L)	1.0	1.4[b]
pH	7.26	typically 7.26

[a]Estimated from alkalinity.
[b]Higher concentrations of Mo and U were used to approximate those used in the Roman Pyrih (undated) study and to provide easily measurable results.

Table 4. Composition of ground water sampled from within the zvi zone and composition of the synthetic ground water (SGW-1453) used in the column test

Constituent	Ground Water From Well 1453 Sampled May 25, 2004	SGW-1453
Sodium (mg/L)	420.0	512.9
Potassium (mg/L)	3.50	3.59
Calcium (mg/L)	1.50	0.00
Magnesium (mg/L)	1.60	0.00
Sulfate (mg/L)	450.0	451.6
Chloride (mg/L)	94.0	94.7
Inorganic Carbon (mg/L)	49.6[a]	50.0
Molybdenum (mg/L)	19.0	0.00[b]
Uranium (mg/L)	0.0014	0.00[b]
pH	10.4	typically 10.4

[a]Estimated from alkalinity.
[b]No Mo or U was added so that any release could be easily observed.

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The initial porosity of the column was 470 mL as determined by the volume of fluid required to fill the ZVI portion of the column. The column was operated from December 6, 2004, through January 20, 2005, during which about 193 pore volumes of fluid flowed through the column. For most of the test, the flow rate was 0.92 mL/min, which corresponds to a residence time of 8.5 h. Various stresses were applied to determine the effects of parameters that might occur in a PRB. These stresses included (1) increasing flow rates to 3.67, 18.4, and 36.8 mL/min, which correspond to residence times of 2.13, 0.43, and 0.21 h, respectively; (2) shutting the system down for extended periods to simulate longer residence times; and (3) increasing the pH values of the influent to more than 10 to simulate the effects on Mo release recently observed in the Cotter PRB. After each stress period, the system was run at 0.92 mL/min to stabilize and observe rebound. Table 5 provides a summary of the conditions during the column tests.

Table 5. Column test conditions; changes of flow rates (residence times) and influent fluid compositions during column operation.

Condition Number	Pore Volume	Residence Time (h)	Fluid Composition	Comments
1	0 – 13.1	2.13	SGW-1455	
2	13.1 – 30.2	8.51	SGW-1455	
3	30.2	65	SGW-1455	Shut down for 65 h
4	30.2 – 43.9	8.51	SGW-1455	
5	43.9 – 47.7	8.51	SGW-1455, high pH[a]	pH 10.2
6	47.7 – 60.8	8.51	SGW-1455	
7	60.8 – 84.0	2.13	SGW-1453	pH 10.4, no U or Mo
8	84.0 – 97.7	2.13	SGW-1455	
9	97.7 – 110.6	8.51	SGW-1455	
10	110.6 – 135.1	0.43	SGW-1455	
11	135.1	14	SGW-1455	Shut down for 14 h
12	135.1 – 166.5	0.21	SGW-1455	
13	166.5 – 191.9	8.51	SGW-1455	
14	191.9	140	SGW-1455	Shut down for 140 h
15	191.9 – 193.0	0.21	SGW-1455	
16	193.0	NA	NA	Final shutdown

[a]SGW-1455 was adjusted to pH 10 with NaOH. Calcium carbonate precipitants were filtered out prior to use.

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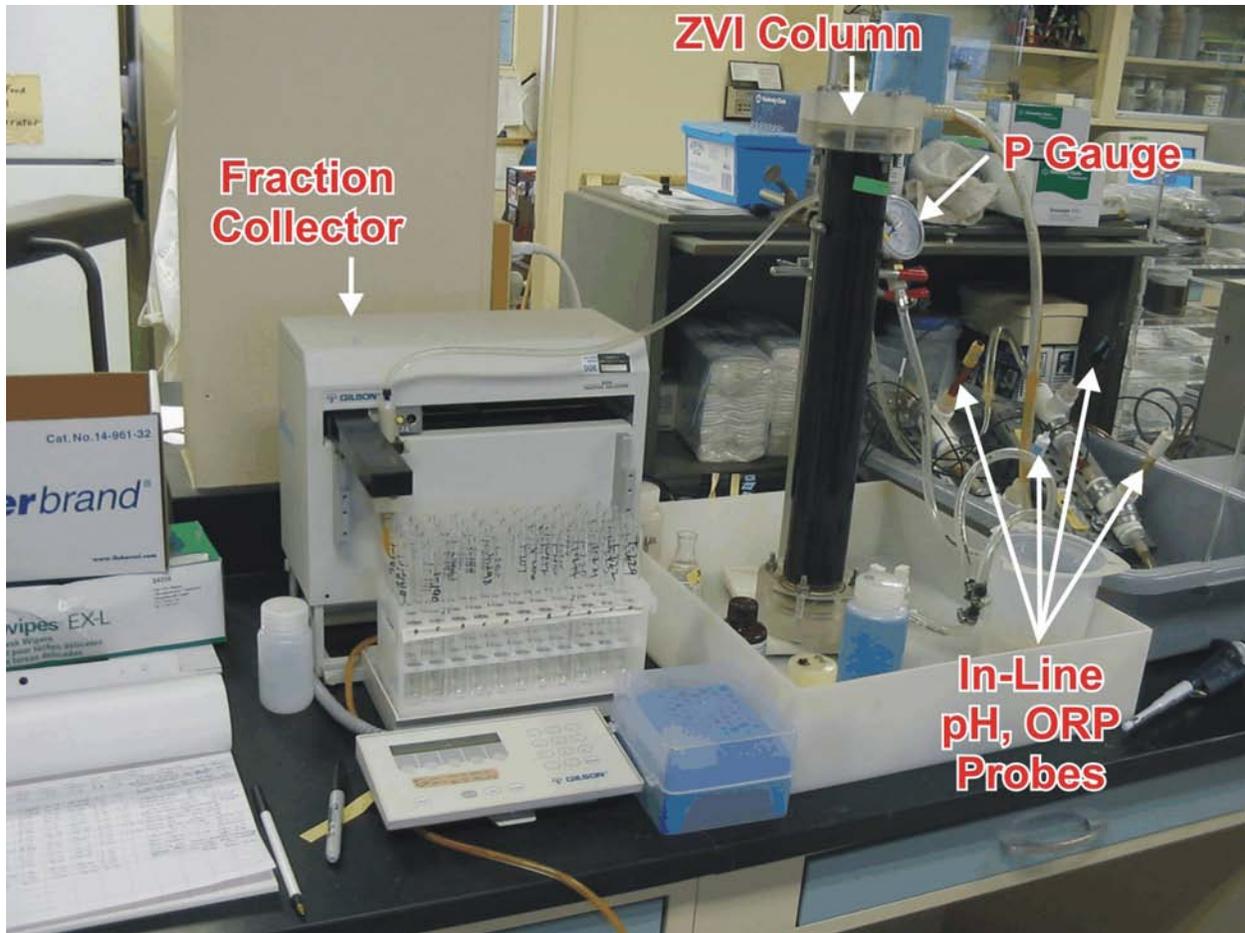
Figure 28. Column test apparatus.

Figure 29 shows the effluent concentrations of Mo and U throughout the column tests. The influent Mo concentration was 8.05 mg/L, other than pore volumes 60.8 to 84.0 when no Mo was added to the source tank (Table 5). During operation at 0.92 mL/min (8.51-h residence time), the Mo concentration in the effluent was less than 1.0 mg/L (88% removal) and, for much of the time, it was less than 0.5 mg/L (94% removal). At increased flow rates, effluent Mo concentrations were higher: 0.9 mg/L for a flow rate of 20 mL/min (residence time 0.43 h), and about 2.8 mg/L for a flow rate of 40 mL/min (residence time 0.21 h). Increasing the influent pH value to more than 10 caused Mo to be released from the column at concentrations to 2.8 mg/L (pore volumes 67 to 84; Figure 30). Effluent U concentrations were less than 0.0002 mg/L for most of the test period, regardless of influent composition or flow rates.

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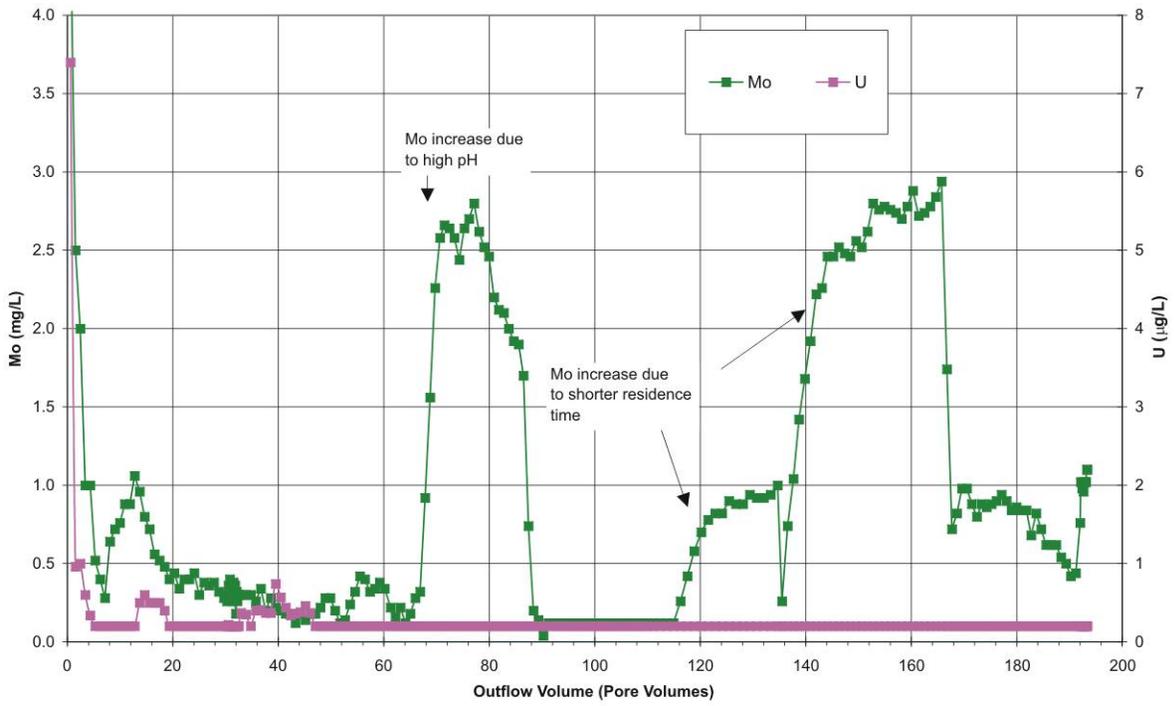
Figure 29. Column test results showing effluent Mo and U concentrations.

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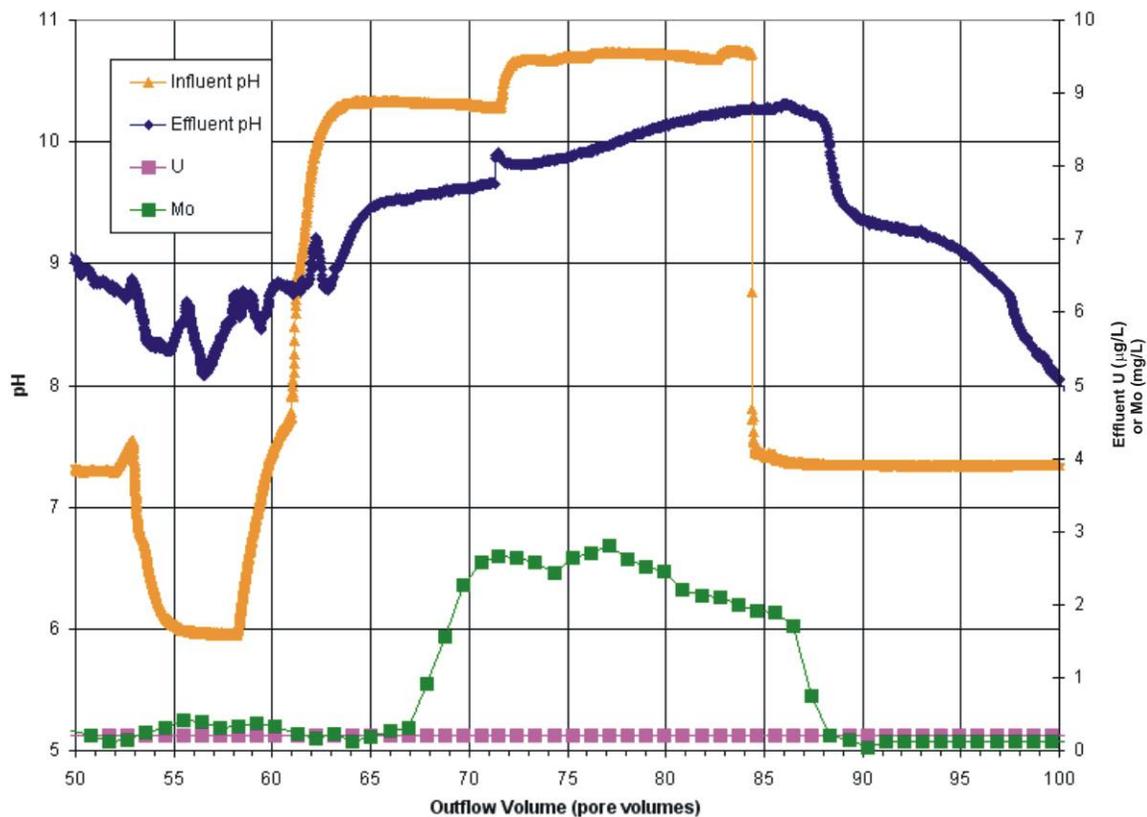
Figure 30. Column test results showing effect of increased pH values on Mo and U concentrations.

Changing the residence times also changes the major-ion composition of the effluent. Increasing the residence time from 0.21 h to 8.51 h results in effluent Ca concentrations decreasing from 160 to 50 mg/L and effluent Fe concentrations decreasing from 50 mg/L to zero (Figure 31). Effluent pH values increased from 7.9 to 9.3 as residence time increased from 0.21 to 8.51 h (Figure 31). The results suggest, for an equivalent volume of ground water treated, porosity plugging is likely to be more severe as residence times increase. On the basis of the volume of water passed through the column and the Ca concentration gradients, an estimated 2.2% of the available porosity was filled by calcium carbonate during the column test.

The observed trends in major ion chemistry are consistent with a model that predicts system response by the irreversible corrosion of ZVI (Morrison et al. 2001). The irreversible corrosion of ZVI consumes aqueous protons, causing pH values to increase. As the pH values increase, Ca precipitates in calcium carbonate minerals. Aqueous Fe concentrations initially increase because of ZVI dissolution, but as the pH values continue to increase (with longer residence time), Fe precipitates as hydroxide phases. This model also explains the lower Ca and Fe concentrations that occur at longer residence times. Therefore, residence time is an important variable when evaluating chemical evolution and potential for pore plugging in ZVI-based PRBs.

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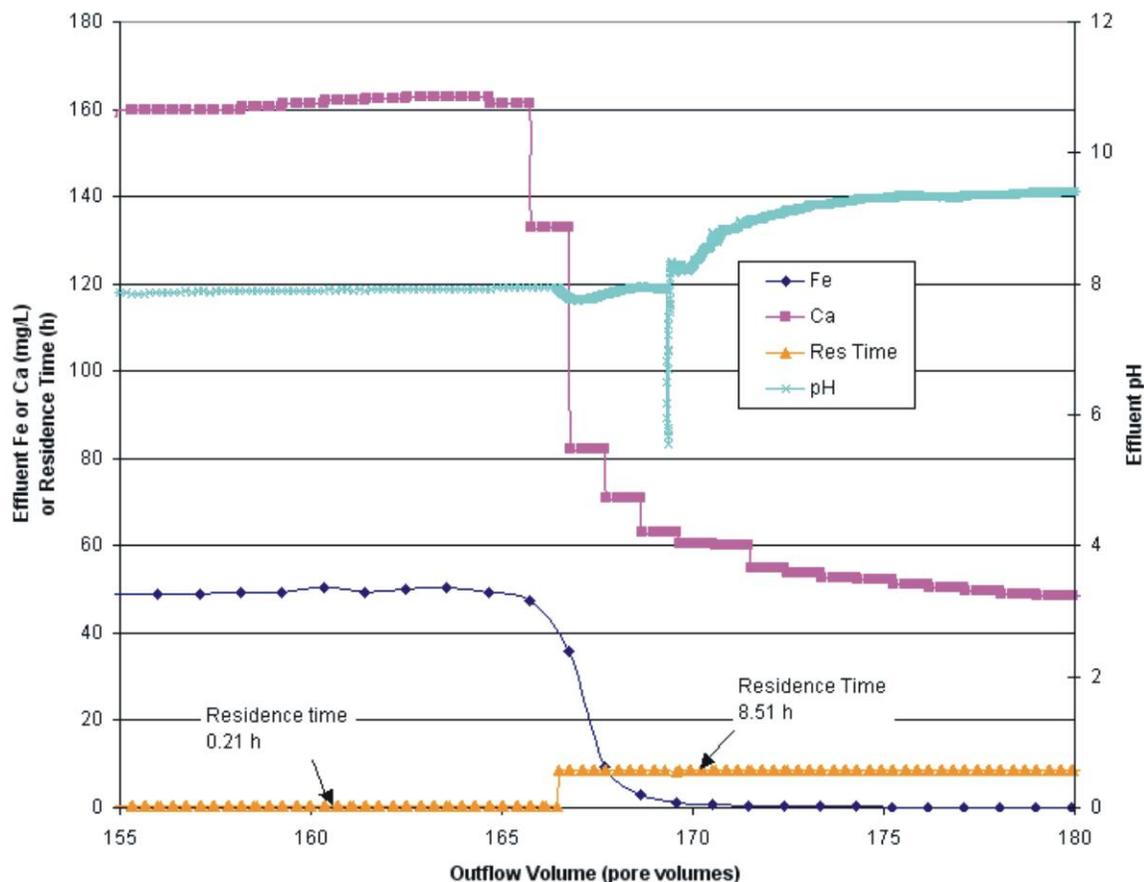
Figure 31. Column study results showing effect of variable residence times on aqueous chemistry. The sudden low pH values near 170 pore volumes were due to an unanticipated depletion of the nitrogen purge gas tank that was immediately replaced.

With one major exception, effluent sulfate concentrations were nearly constant during the column test. Following a 140-h shutdown at pore volume 191.9, sulfate concentrations decreased from influent values of about 1280 mg/L to a minimum of 783 mg/L (Figure 32). Following earlier shutdown periods for 65 and 14 h, no detectable decreases in sulfate concentrations were observed. However, hydrogen sulfide odors were emitted from the effluent samples at various times during the test. A few samples were analyzed for aqueous sulfide, but no sulfide was detected. No sulfide was detected in samples analyzed following the 140-h shutdown either, suggesting that sulfide, if it was produced, was rapidly combined with Fe in ferrous sulfide minerals. Low effluent sulfate concentrations following the 140-h shutdown period are likely due to sulfate reduction by microorganisms. As indicated by BART (Hach Company) tests, sulfate reducing bacteria were present in the column effluent following the 140-hour shutdown period. Sulfate reduction is also likely occurring in the Cotter PRB, as indicated by the abundance of sulfide measured in the EM study (see previous section of this report).

Immediately following the shutdown values of pH were low, probably because of an experimental artifact, perhaps oxidation in the outlet tubing. The pH values increased rapidly to about 9.5, which is likely closer to the actual pH value that existed in the column during shutdown. Concentrations of Mo increased, but only slightly, following shutdown (Figure 32).

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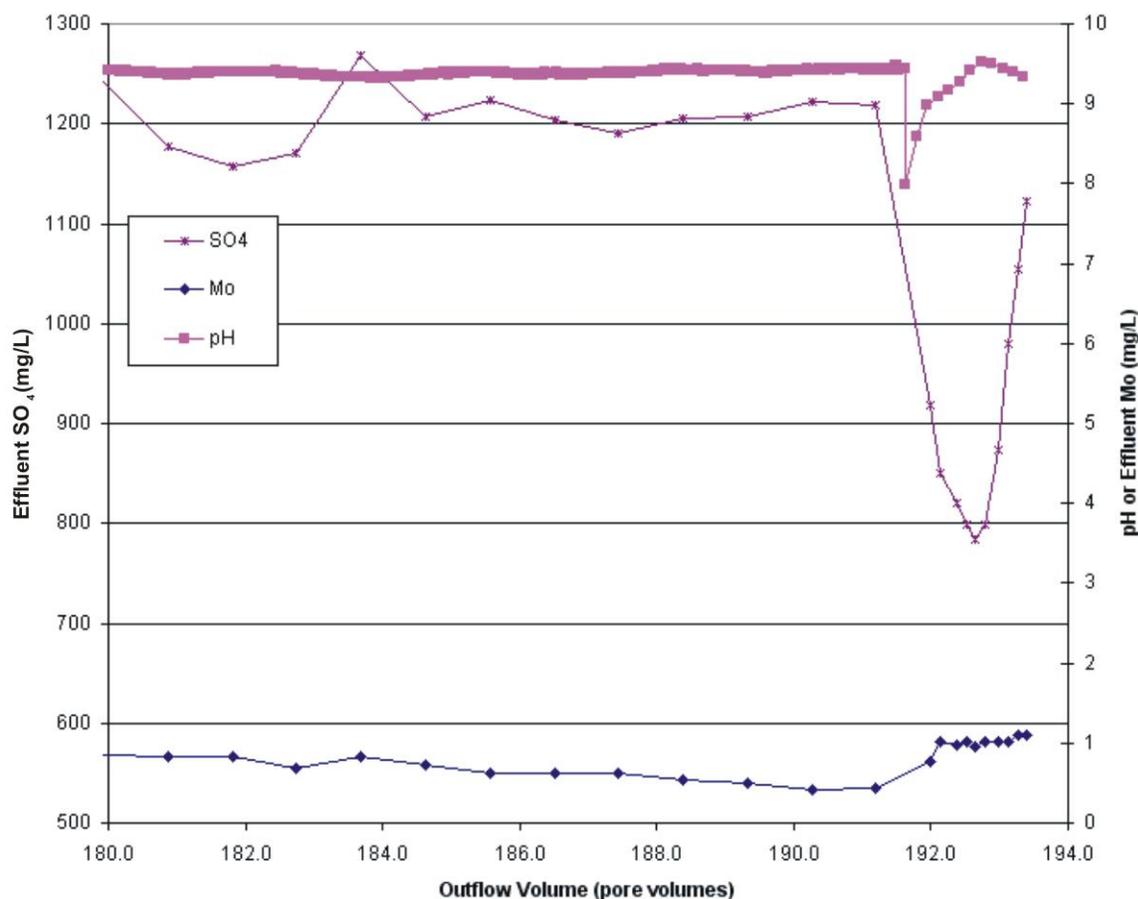
Figure 32. Column test results showing effect of a 140-h shutdown at pore volume 191.9.

6.0   Summary and Conclusions

The PRB at Cotter's Canon City millsite functioned well for a period of 0.5 to 1 year following installation. Uranium concentrations were reduced from about 1 mg/L to less than 0.0002 mg/L and Mo concentrations were reduced from about 8 mg/L to less than 0.2 mg/L. Evidence from the current study, as well as a review of data from two previous studies, indicate that Mo removal from ground water by ZVI is effective but slower than for U.

As ground water flowed through the PRB, the ZVI corrosion process caused minerals to precipitate in the pores, resulting in progressive reduction of hydraulic conductivity. Mineral precipitation was particularly intense within 0.5 ft of the front face of the ZVI but continued to some extent throughout the ZVI zone. Mineralization includes large crystals of aragonite ($CaCO_3$) filling or partially filling pore space and overgrowth rims consisting of iron (hydrous) oxides, sulfides, and aragonite. Uranium and Mo are concentrated in rims that coat other corrosion products. These rims are often rich in sulfides and oxides.

After about one year of operation, hydraulic conductivity was significantly reduced, as evidenced by ground-water mounding upgradient of the PRB. By early 2004, chemical signatures indicate that most of the ground water was bypassing the ZVI or was flowing through preferential

pathways and not being treated. Three noteworthy changes had also occurred in the PRB: (1) pH values increased to more than 10, (2) sulfate reduction was initiated or became much more pronounced, and (3) Mo concentrations in ground water within the ZVI increased to values higher than in the influent ground water. Decreases in hydraulic conductivity have been noted in other ZVI-based PRBs. During the first 5 years of operation of the Monticello PRB, hydraulic conductivity in the ZVI decreased by an order of magnitude, as evidenced by the results of repetitive gas-injection slug tests on more than 40 wells (DOE 2005). Much of the decrease is attributed to precipitation of calcium carbonate and other corrosion products (Morrison, 2003).

Despite the high concentrations of Mo measured in ground water samples from the PRB, column test data suggest that the ZVI is still capable of removing Mo and U from solution. The elevated pH value is probably responsible for the high Mo concentrations in the PRB. Increased pH values are caused by corrosion of ZVI as exemplified by Reaction 1.

$$Fe^0 + 2H^+ = Fe^{2+} + H_2 \qquad\qquad \text{Reaction 1}$$

Values of pH may be increased even further as ZVI provides H_2 for biogenic sulfate reduction (Reactions 2). Note that H_2 is produced by the corrosion of ZVI (Reaction 1) and is consumed by sulfate reduction (Reaction 2). The overall reaction, combining Reactions 1 and 2, consumes 8 mols of protons per mol of sulfate that is consumed to form ferrous sulfide, FeS (Reaction 3).

$$4H_2 + SO_4^{2-} + Fe^{2+} = FeS + 4H_2O \qquad\qquad \text{Reaction 2}$$

$$4Fe^0 + 8H^+ + SO_4^{2-} = 3Fe^{2+} + FeS + 4H_2O \qquad\qquad \text{Reaction 3}$$

As mineral matter precipitated in the pores, ground-water flow gradually slowed and residence times increased. The longer residence times caused the ZVI corrosion reaction to proceed further and the pH value to increase. In addition, long residence times may accentuate the populations of sulfate-reducing bacteria. Sulfate reduction has been noted in other ZVI-based PRBs (Rowland 2002; Gu et al. 2002).

Ground water bypass and preferential flow has been noted in other ZVI-based PRBs. Using detailed ground water tracer data from a PRB at a solvent recycling site in Denmark, Lai et al. (2004) showed that preferential paths caused by mineral precipitation had developed in the ZVI. Birke et al. (2004) report that at least two of three full scale systems in Germany have hydraulic problems such as bypassing ground water because of mineral precipitation in the ZVI. These authors recommend accessible PRB systems that enable regular maintenance.

6.1   Conceptual Model of Molybdenum Uptake in the Cotter PRB

On the basis of these observations, the evolution of Mo uptake by ZVI in the PRB is explained in four stages (Table 6). In Stage 1, ground water passed through the PRB as porous media flow. This stage occurred from the time of the PRB construction in June 2000 until about February 2001, a period of about 250 days during which about 219 pore volumes passed through the PRB (assuming ground-water flux of 1 gal/min). This stage is characterized by an average residence times of about 56 h if ground-water flux is 1 gal/min or about 19 h if the ground-water flux is 3 gal/min (possibly closer to the actual flux following construction of the PRB). Molybdenum was

efficiently removed from the ground water, resulting in concentrations of less than 0.2 mg/L. High concentrations of Mo in the solid phases indicate that at least some of the Mo was precipitated as Mo mineral phases, although some may also have been adsorbed to mineral surfaces. The water table was flat across the ZVI and both sand zones.

Table 6. Conceptual four stage model of Mo uptake in Cotter PRB

Stage	Dates	Mo (mg/L)	Water Table	Characteristics
1	June 2000 – Feb 2001	<0.2	Flat across PRB.	Porous media flow.
2	Feb. 2001 – Nov. 2001	Steady increase <0.2 to 4	1 ft in UGS; ZVI, DGS flat	Preferential flow paths forming.
3	Nov. 2001 – Jan. 2003	2 to 4	4 ft in UGS; ZVI, DGS flat. Starting to rise in ZVI.	Preferential flow continues; pH steady, 7.5; Ca decreasing.
4	Jan. 2003 – Oct. 2004	19	4 ft in UGS; 2 ft in ZVI	Bypass. Stagnant in ZVI. Ca < 10 mg/L, pH >10, SO_4 decreasing rapidly.

UGS = upgradient sand, DGS = downgradient sand

Stage 2 occurred from approximately February 2001 to November 2001, a period of about 270 days during which 232 pore volumes flowed through the PRB (at 1 gal/min). During Stage 2, the water levels were flat across the ZVI and downgradient sand, but the level in the upgradient sand increased to a height about 1 ft above the level in the ZVI. Molybdenum concentrations in the ZVI steadily increased from less than 0.2 mg/L at the beginning of Stage 2 to about 4 mg/L. This period is characterized by the development of preferential flow paths through the ZVI that decreased the residence time. On the basis of Mo removal rates from the column test, the effective residence time was probably less than a few hours.

Preferential flow through the ZVI continued through Stage 3 which lasted from November 2001 to January 2003, a period of 420 days (361 pore volumes at 1 gal/min). Molybdenum concentrations in the ZVI were relatively constant, between about 2 and 4 mg/L, throughout Stage 3. The water table in the upgradient sand increased rapidly and reached a maximum of about 4 ft above the water level in the ZVI. The pH values in the ZVI were nearly steady at 7.5; however, Ca concentrations began to decrease, indicating a trend toward longer residence times.

Stage 4 occurred from January 2003 through the time of this study in October 2004. Ground water was bypassing the ZVI or moving through preferential pathways in Stage 4. Ground water in the ZVI was nearly stagnant, yielding very long residence times. The ground-water level in the ZVI increased to an elevation about 2 ft above the level in the downgradient sand, indicating that hydraulic conductivity in the ZVI was decreasing. Chemical indicators of longer residence time include decreased Ca and Mg concentrations to nearly zero and increased pH values to more than 10. Sulfate concentrations in the ZVI were significantly lower than in the incoming ground water because of precipitation of sulfide minerals. Sulfate-reducing bacteria were likely accelerating sulfate reduction and the process was probably aided by the nearly stagnant water. Molybdenum concentrations in the ZVI increased to as high as 19 mg/L during Stage 4 in response to the high pH value. Molybdenum that was previously precipitated was redissolved. The flux of Mo-rich ground water from the ZVI was probably minimal because the rate of ground water flow from

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the ZVI was minimal. However, the PRB was not effectively remediating ground water because of the bypass.

7.0   Recommendations

One of the objectives of this study was to gather data to help make sound decisions on the future operation and/or disposition of the PRB. Several recommendations are made that could improve the performance of the PRB so that ground-water standards would be met. Two factors which must be addressed to improve the ability of the Cotter PRB to meet ground-water standards include: (1) how to rejuvenate or rebuild the PRB to make it functional again and (2) how to maintain it so long-term treatment costs are minimized.

It is beyond the scope of this investigation to provide detailed designs or to completely evaluate the cost effectiveness of any method. Rather, the recommendations are conceptual in nature and will require additional effort to evaluate development and implementation costs. In most cases, these ideas have not been tested elsewhere and, thus, an inherent economic risk exists in conducting technology development efforts. The recommendations are listed in decreasing order of the amount of technology development required.

7.1   Install Accessible Treatment System

Although, many aspects of PRB systems are well understood, there are still significant uncertainties in their overall performance because of the limited amount of operational experience in industry. In fact, no other sites specifically treat Mo in PRBs. Because of this lack of experience, it is likely that system modifications will be required for some time into the future until there is sufficient operational experience to have confidence to allow the system to function passively with limited intervention. A system that can be accessed and easily modified would lessen the high costs associated with excavating, repairing and/or replacing inaccessible subsurface systems.

Three accessible systems are in operation at the DOE Rocky Flats site near Denver, Colorado. These systems have been operating with relatively little modification for several years (verbal communication with Annette Primrose). Two others accessible systems operated for several years at DOE's Durango Bodo Canyon site (Morrison et al. 2002b). These systems require some regular maintenance, but the amount of ZVI is typically less than in passive PRBs and capital costs are usually much less. Only two samples (inflow and outflow) are required for complete performance evaluation because the ground water is piped. These systems generally consist of a container such as a tank containing ZVI. Ground water is piped into the tank and accurately metered. Flow rates can be controlled and the system can be accessed to conduct maintenance such as breaking up crust that forms on the ZVI.

7.2   Acid Rejuvenation

On the basis of the qualitative results previously discussed, treatment of the ZVI from the PRB with HCl is effective in removing the corrosion products. The ZVI after washing in HCl was similar in appearance to fresh ZVI. Thus, one option is to attempt treatment of the PRB with HCl (or muriatic acid, its common commercial form, which is approximately 30% concentrated HCl).

While this type of treatment may be viable from a chemical perspective, issues involving delivery to the PRB may be problematic. Injection of the acid into the upgradient sand may be a means of delivering the acid to the front of the PRB where the porosity plugging is most severe. The acid will likely dislodge particles of other corrosion minerals as the carbonate dissolves. These particles need to be removed to avoid producing additional clogging. Complete evaluation of the delivery and recovery system is beyond the scope of this study.

An estimate of the acid consumption was made to help evaluate costs of conducting acid treatment. For this estimate, it was assumed that all the Ca deposited in the PRB as calcium carbonate and that most of it had to be removed. Two mols of acid are needed to remove 1 mol of calcium carbonate. Removal of the 1,881 kg of calcium carbonate estimated to be within the PRB based on the bulk chemical analyses requires 823 gal of concentrated (12.1 N) HCl or 2,742 gal of muriatic acid. Cost of the muriatic acid is about $5,500.

Other issues with acid flushing include gas production and acid disposal. Acid flushing will produce carbon dioxide and hydrogen gases. Care must be taken to avoid excessive frothing or geysering through the wells. The acid will likely redissolve some contaminants and would likely require extraction and disposal. Wells in the downgradient sand could be used for extraction.

7.3   Install Pretreatment Zone

Pretreatment zones, using a mixture of gravel and ZVI, have been used with some PRBs (e.g. Morrison et al. 2000a). The function of a pretreatment zone is to decrease dissolved oxygen levels and to remove some of the mineral matter before the ground water enters the ZVI zone. Because the pores in the pretreatment zone are larger than those in the ZVI zone, precipitation of the mineral matter does not decrease hydraulic conductivity as rapidly as it does in ZVI. Thus, the longevity of the PRB is improved. Installation of a pretreatment zone would require major construction, probably including removal and rebuilding of the entire reactive zone.

Another alternative would be to install a cation exchanger as a pretreatment. If Ca in the ground water could be exchanged for sodium, no calcium carbonate minerals would be precipitate. Interaction with ZVI should not cause sodium to precipitate.

7.4   Control Microbial Activity in the PRB

To our knowledge, control of microbial activity in a PRB has not been attempted. The processes in the Cotter PRB that remove U and Mo are likely abiotic and not affected by microbes. However, sulfate-reducing bacteria may be responsible, at least in part, for the increases in pH values that are causing Mo to be released. Sulfate reduction is also causing precipitation of iron sulfide minerals further contributing to loss of hydraulic conductivity. Routine control of biofouling in water wells is accomplished by adding chlorine bleach or other compounds that can help destroy the microbial populations. A similar application may be possible for the PRB. These treatments would not rejuvenate the PRB, but might be helpful in maintaining it.

7.5   Ultrasonication

Cotter has considered using ultrasonication to rejuvenate the PRB. Ultrasonication has been used in laboratory studies to remove corrosion products from the surfaces of ZVI. Application of

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ultrasonication to a ZVI-based PRB in Florida improved reaction rates for chlorinated solvents up to 67% (Geiger et al. 2002). No tests of sonication were conducted during this investigation. Because of the hard and rigid nature of the ZVI within the Cotter PRB and observations of the mineral habits, it seems unlikely to us that sonication could significantly improve hydraulic conductivity.

8.0   Acknowledgments

9.0   References

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U.S. Department of Energy
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Appendix A

Chlorine in 1094
    Full strength - turned cloudy
        $Cl = 1.72$
With 10x dilution - clear (pink) not cloudy
reading $Cl = 0.27$ (2.7 actual)
                   mg/L
  No chlorine added.
  Removed filter (1094) - looks clean.
  Replaced it (same filter).
  Filter is leaking (it was leaking
    before I started too). Needs to
  be replaced - could be big job.

✓14:30 Called Brandon. He contacted
Campbell. We set "address" to 5
and were able to download the
remaining data.

15:30 @ 1087 (BLW)
TOTAL 1 = 137054
TOTAL 2 = 10964
   CHLORINE = 0.62 mg/L

16:17 Added ½ gal Aqua chem pellets
  to BLW sump.

16:44 @ 1070. Removed filter - it
was very clean. Just a few
flakes of scale (loose); washed
them off and put same filter
back in.

10/8/04 Cotter Corp. Millsite @
Canon City, CO. Preston Niesen,
Paul Muskovic + 3 contractors.
   Using backhoe & trench box
to cut trench across the PRB
at the west end. Right through
the 3 well + 3 lysimeters (these
were sacrificed.

15:30 Top of ZVI was exposed when
Paul and I arrived - top 20 ft so
so of fill had been scraped off.
   Immediately overlying the
ZVI was 3 ft of clay - Preston
said it was wet clay.
   Top is 7 ft from hypalon
(hypalon is at the base of the ZVI)
This 7 ft thickness of ZVI was

determined by using a tape measure in the abandoned (pulled) well hole. The wells and lysimeters were pulled with the trackhoe. The wells/lys in the sand layers (it is a fairly well sorted, coarse sand) pulled easily. The ones in ZVI (both in the middle of the ZVI) broke off.

PLAN VIEW
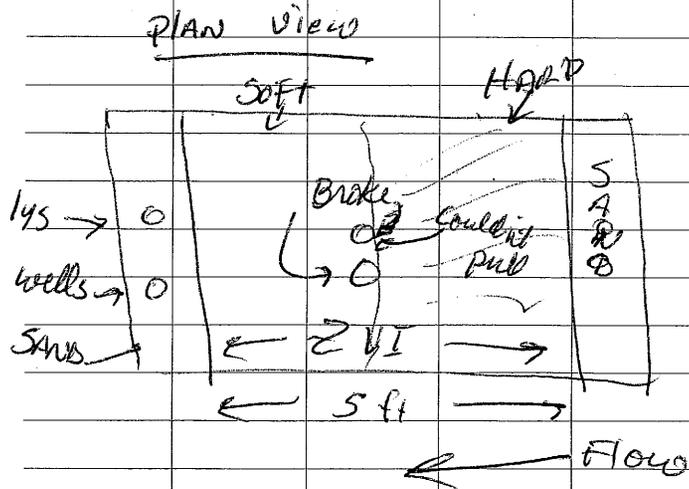
The front (up gradient) portion of the ZVI is very hard. Downstream side is soft (relatively). ZVI zone is 5ft wide. 2½ ft are

very hard (about ½ of the ZVI zone). It was so hard, they couldn't break it with the hoe bucket. Preston tried a pick and then a hammer/chisel. Was able to get a few samples – very tough. Took photos.

Samples ✓ height (ft)

COT – 6.9 – 3.5

Cross-Section

Sample List

COT – 6.9 – 3.5 (no Carb – HCl)
COT – 7.0 – 0.0
COT – 6.5 – 0.0
COT – 7.0 – C.0A
(sample is from front face – embedded sand grains)
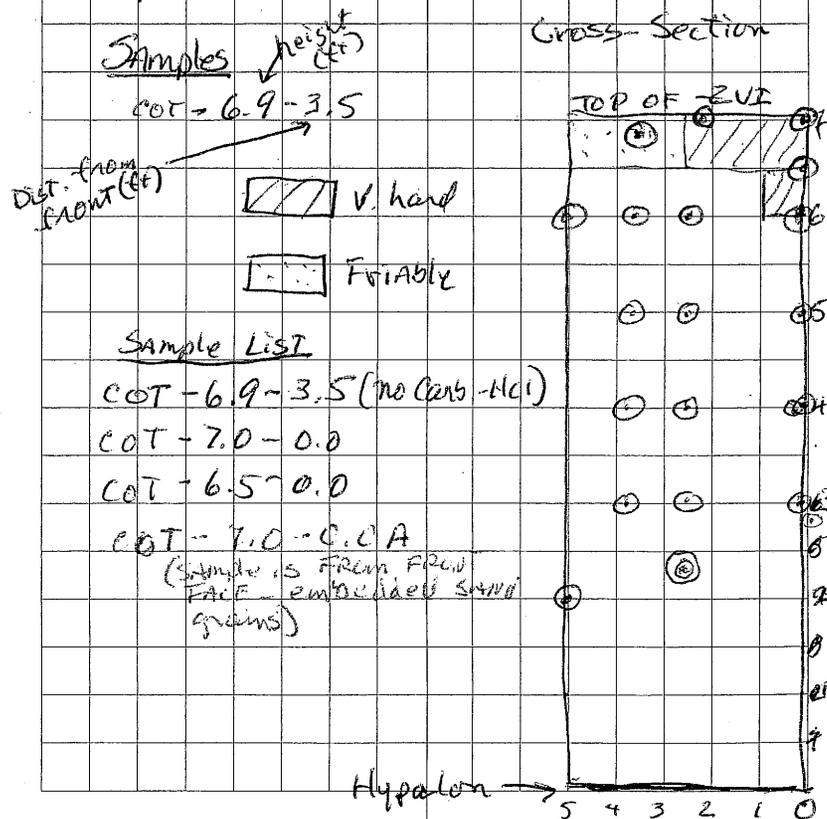
Found carbonate at the immediate
leading edge (1/2") of the ZOI.
(This is in the upper 6" only - that
is all we have exposed.)
  Other samples do not have
carbonate.

10/13/04   07:00 Raining hard.
  08:00 Mel Preston and
    2 State people Phil Stoffey
  and Edgar?) at Cotter office.
Discussed various options including
deploying new reactive materials.
  Preston concerned about inability
of PRB to contain Mo and
with the hard layer. Mushovic
very interested in the hard layer.
  We plan to take 27
samples on grid front, mid, back
from each of 1' layers (7 total
layers). Plus, discretionary
samples. This is much in
excess of our original plan
of 9.

Will take 6 samples in
jars for EM/SEM. Need
to locate an SEM (should
mount chunks to see sutures
points that cause hardness).
  The 6 samples will be from
the lower horizon where more
Mo likely.

10/27/04 7:30 AM Paul and I arrived
at Cotter mill site to start excavation

CCT-7.0-0.0
LiFT I
0-1"
starting at
top of ZOI

CCT-7.0-0.0A
(large size)
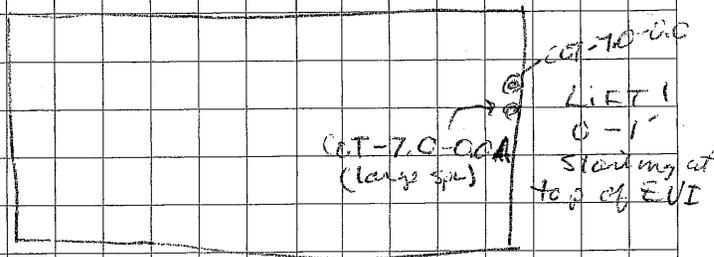
CCT-7.0-2.5 (sample includes top surface)
                Top is 2mm of ferric oxide

CCT-7.0-0.0 R   (R = research sample)
CCT-7.0-0.0RA (has greenish material
                $Fe(OH)_2$?)

COT-6.0-0.0R (ACC FIZZ)
    This sample is very characteristic
    of the permeability loss at snow
    edge.

COT-6.0-0.0 }
COT-6.0-2.5 } Bulk chem. samples
COT-6.0-3.5 }

COT-6.0-5.0 From contact at gravel.

10:14 Lift 5.0 was hard even at 2.5 ft
    from face. Trouble pounding through
    it with backhoe jackhammer.

COT-5.0-0.0 }
COT-5.0-2.5 } Bulk samples
COT-5.0-3.5 }

COT-5.0-0.0R } Representative
COT-5.0-2.5R }   samples

*COT-4.0-0.0 }
*COT-4.0-2.5 } Bulk samples
COT-4.0-3.5 } (still dry)

* Sample effervesced

COT-4.0-0.0R From front of PRB
    (Should show mineral zone)
      strong fizz
COT-4.0-2.5R
COT-4.0-0.1R Same as COT-4.0-0.0R
    But 2" in. Has grains (weathering?)
    of amyg. translucent mineral. At
    first I thought they were qtz
    grains.

15:32 Sampled 3 ft lift
    COT-3.0-0.0 }
    COT-3.0-2.5 } Bulk samples
    COT-3.0-3.5 }

COT-3.0-0.0R Front of wall

15:40 Hit water at 2.9 ft (from bottom)
                    of ZVI
    Collected front sand zone sample
    COT-2.9--1.0 (sand sample)

COT-2.0-5.0 Hard ZVI at
    back of PRB. Looks to have
    low permeability. Specular hem.?

17:00 Collected large sample for possible column tests.
COT-2.3-2.5 (1 Full Bag)
This sample has greenish material (green rust). Amygdaleadal translucent grains ADD. Sample mostly Crumbly. v. BLACK. Probable pyrite.

10/28/04 8:04 AT CUTTER P2D site
Waiting on pump. Saron called - said we need B-8 scans
Once Pump arrived. SANDPIPER.
Uses compressed air to actuate diaphragm

Samples
COT-2.0-0.0
COT-2.0-0.0 R
YOT-2.0-5.0
COT-2.0-5.0 R
COT-2.0-2.5 } ZVI covered w/
COT-2.0-2.5R } "Fungus" like minerals

COT-2.0-0.0 RA   Front 1" Ahead of the ZVI. Well cemented. Broke off front face as slab Cemented gravel sand.

HAS qtz grains covered w/ Black coatings.

COT-2.0-1.0
COT-2.0-3.2

COT-1.0-2.5 } Fungus like min.
COT-1.0-2.5 R } Black, loose.

COT-1.0--0.1   Gravel (SAND) Black cemented. Front of ZVI (FLAKED OFF)

COT-1.0-1.0   } v. cemented, high fee,
COT-1.0-1.0 R } probable pyrite
COT-1.0-0.5
COT-1.0-0.5 R

COT-1.0-5.0+   SAND w/ BLACK coating. From SAND PACK

COT-1.0-5.0   Fungus like minerals Quite impermeable

COT-1.0-0.5 A
COT-1.0-0.5 RA

COT-1.0- -0.2 SAND, thick
      piece of BLK - cemented sand?
   Flat is the cement wall

COT-1.0- 0.0 Large piece of
      front of PRB

COT-1.0- 0.0 R

17:00 small glass jars were
   purged w/ N₂ and
   capped tightly.

19:15 Left site after getting
   rad counts on samples.

11/17/04 Met Hoppins at Moab
at 11:15 Am. Briefed on use
of downhole ↓ probe. Met
Bob Schlosser at Monticello
about 1 pm. ↓ logged 3
wells in grav/ZVI. Had
to use geoprobe Rod to get
↓ sonde to bottom.
      Picked up detectable
signals in bottom of wells.
We should do this on all wells.
      Bob S. is conducting gas-
injection, hyd. cond. tests.
Most wells have lower HC
than previous year.

Appendix B

Cotter Solid Samples

1	2	3	4	5	6	7	8	9	10	11	12	13

10-29-04 15:51 Placed glass bottled samples in small ice chest under N_2 atmosphere 3 L/min.

Weighed and inventoried samples. Excel spreadsheet on laptop "solid samples xls"

ALL "R" (research) samples in glass jars are kept under N_2.

10/31/04 ~ 11/1/04 Took photos with Wild Stereo microscope. Fibrous xtals

11/1/04 11:27 Placed COT-1.0-1.0 R split, called it COT-1.0-1.0 R, Split + S1

Drying Research under vacuum, w/ Drierite.
Samples

Sample	Time	Weight (w/ jar)	Water loss (g)						Vacuum Jar	glass jar		
COT-1.0-1.0R, S1	11:32 11/1/04	158.082 g							Sample	Plastic vessel		
	15:24	154.828 g	3.25									
	16:49	154.764 g	3.31 g									
COT-1.0-0.0R-S1	11/3/04 7:19	159.498 g										
	10:03	156.029 g	3.47 g									
	12:27	155.495	4.00 g									
COT-1.0-0.5RA-S1	12:37	146.626										
	13:36	144.964	1.66 g									
	13:52	144.472	2.15 g									
	15:52	143.148										
COT-1.0-0.1-S1	16:09	173.733 g										
	16:49	171.229										
	17:27	170.46 g										

MISC-01-13-02

Microwave Digestion - Cotter Mill Samples Mending Experiments

11/1/2004 — Obtain samples from Cotter Mill. Rad area established. Dry ~30g split of each in oven @ 105°C. Two sets of samples repeated in triplicate. Check weight at 4 hours and again at 18 hours. Four hours appears to be adequate drying time. Note each of triplicate samples obtained from laurel split in very close proximity. The "SD" samples are taken at the interface where gravels are present. No sands are included!

Perform microwave digestion (ESL proc. manual SE(MD-1)) using 0.5g sample. Final dilution of all digestates was 50mL

See attached spreadsheet for drying details, results, comments on samples

Perform ESL analysis of all samples for U. On 5 only for Mo.

Send all digestates to Paragon Labs for Mo analysis. U analysis to be performed on 6 highest U result samples in ESL to confirm.
Paragon RIN# 0410135   PO# 24314   Sample ticket #'s   NDZ 226 → 262
Samples received @ Paragon 11/10/2004 0946

Mending Experiments - Cotter Mill Microwave

Sample		Mass		Comments	6	7	8	9	10	11	12	13
	1	(g) Microwave										
OT:	3											
1.0-0.5	4	0.497										
1.0-1.0	5	0.482										
.0-2.5	6	0.487										
1.0-5.0	7	0.494										
1.0-5.0+	8	0.482										
2.0-1.0	9	0.487										
2.0-2.0	10	0.495										
2.0-2.5	11	0.497	sl. white evaporite									
2.0-3.2	12	0.499										
2.0-5.0	13	0.490										
2.3-2.5	14	0.482										
2.9--1.0	15	0.500										
3.0-2.5	16	0.498										
3.0-3.5	17	0.486										
4.0-2.5	18	0.498										
4.0-3.5	19	0.499										
5.0-2.5	20	0.496										
5.0-3.5	21	0.493										
6.0-2.5	22	0.500										
7.0-2.5	23	0.490										
1.0--0.1	24	0.491	gravel present - h. grade for split. omit gravel									
1.0-0.0#1	25	0.498										
1.0-0.0#2	26	0.495										
1.0-0.0#3	27	0.496										
2.0-0.0A#1	28	0.500	gravel present, omit from sample split for digestion									
2.0-0.0A#2	29	0.498	" " " " " "									
2.0-0.0A#3	30	0.499										
3.0-0.0	31	0.493										

MISC-01-13-04

Sample	1	Mass (g) Microwave	3	Comments	6	7	8	9	10	11	12	13
4.0-0.0		0.496										
5.0-0.0		0.498		Some gravel — omit for sample for digestion								
6.0-0.0		0.498		rad when wet, ≤ Bkg when dry								
6.0-5.0		0.498		rad when wet, ≤ Bkg when dry								
7.0-0.0A		0.495		"								
7.0-0.0		0.500		"								
.0-0.0S		0.494		@ contact ē sand								
2.0-0.0AS		0.496		" " "								
4.0-0.0S		0.493		" " "								

Sample	U ug/L Paragon	U ug/L ESL
COT 1.0--0.1	32000	33036
COT 1.0-0.0 #2	32000	43875
COT 2.0-0.0A #1	41000	42000
COT 2.0-0.0A #2	47000	49948
COT 2.0-0.0A #3	33000	35200
COT 1.0-0.0 S1	37000	39588

LAB Comparisons

	Mo ug/L Paragon	Mo ug/L ESL
COT 1.0--0.1	36000	31000
COT 1.0-0.0 #1	18000	16100
COT 1.0-0.5	6100	7200
COT 2.0-0.0A #1	49000	46700
COT 2.0-1.0	4700	3400

	A	B	C	D	E	F	G
1	EPA Cotter Mill Permeable Wall						
2	Sampled 10/2004						
3	Microwave Digestion (0.5g in 10 mL Conc T.M. grade Nitric Acid, dilute to 50 mL)						
4							
5							
6	Sample	Ca	Ca	U	U	Mo	Mo
7		(mg/L)	(ug/g)	(ug/L)	(ug/g)	(ug/L)	(ug/g)
8		ESL		ESL		Paragon	
9							
10	1.0-0.5	154.5	15450	273.5	27.35	6100	610
11	1.0-1.0	70	7000	<50	<5	2600	260
12	1.0-2.5	204	20400	142	14.2	3900	390
13	1.0-5.0	80.5	8050	<50	<5	3800	380
14	1.0-5.0+	0.24	24	<50	<5	22	2.2
15	2.0-1.0	187	18700	<50	<5	4700	470
16	2.0-2.0	374	37400	<50	<5	4300	430
17	2.0-2.5	196	19600	<50	<5	4500	450
18	2.0-3.2	406	40600	<50	<5	4100	410
19	2.0-5.0	55	5500	<50	<5	3200	320
20	2.3-2.5	188	18800	<50	<5	2000	200
21	2.9--1.0	1.49	149	<50	<5	27	2.7
22	3.0-2.5	19.6	1960	<50	<5	3000	300
23	3.0-3.5	121.5	12150	<50	<5	2400	240
24	4.0-2.5	3	300	83	8.3	2000	200
25	4.0-3.5	0.19	19	<50	<5	1300	130
26	5.0-2.5	<0.1	<0.5	<50	<5	1900	190
27	5.0-3.5	<0.1	<0.5	<50	<5	2300	230
28	6.0-2.5	<0.1	<0.5	<50	<5	2400	240
29	7.0-2.5	<0.1	<0.5	35	3.5	2000	200
30	1.0--0.1	207	20700	33036	3303.6	36000	3600
31	1.0-0.0 #1	375	37500	22472	2247.2	18000	1800
32	1.0-0.0 #2	225	22500	43875	4387.5	19000	1900
33	1.0-0.0 #3	650	65000	19776	1977.6	22000	2200
34	2.0-0.0A #1	257	25700	42000	4200	49000	4900
35	2.0-0.0A #2	309	30900	49948	4994.8	53000	5300
36	2.0-0.0A #3	362	36200	35200	3520	35000	3500
37	3.0-0.0	442	44200	2089	208.9	3900	390
38	4.0-0.0	59.4	5940	8323	832.3	8000	800
39	5.0-0.0	186	18600	13284	1328.4	29000	2900
40	6.0-0.0	35	3500	223	22.3	2200	220
41	6.0-5.0	<0.1	<0.5	<50	<5	1800	180
42	7.0-0.0A	<0.1	<0.5	<50	<5	2900	290
43	7.0-0.0	<0.1	<0.5	<50	<5	3000	300
44	1.0-0.0 S1	206	20600	39588	3958.8	41000	4100
45	2.0-0.0A S1	190	19000	21948	2194.8	25000	2500
46	4.0-0.0 S1	93.4	9340	28120	2812	41000	4100

	A	B	C	D	E	F	G	H	I
1	EPA Cotter Mill Permeable Wall								
2	Sampled 10/2004								
3	Microwave Digestion (0.5g in 10 mL Conc T.M. grade Nitric Acid, dilute to 50 mL)								
4								ESf	
5									
6	Sample	Analytes	ACL #	Ca	Ca	U	U	Mo	Mo
7				(mg/L)	(ug/g)	(ug/L)	(ug/g)	(mg/L)	(ug/g)
8									
9									
10	1.0--0.1	Mo, U	226	207	20700	33036	3303.6	31	3100
11	1.0-0.0 #1	Mo	227	375	37500	22472	2247.2	16.1	1610
12	1.0-0.0 #2	Mo, U	228	225	22500	43875	4387.5		
13	1.0-0.0 #3	Mo	229	650	65000	19776	1977.6		
14	1.0-0.5	Mo	230	154.5	15450	273.5	27.35	7.2	720
15	1.0-1.0	Mo	231	70	7000	<50	<5		
16	1.0-2.5	Mo	232	204	20400	142	14.2		
17	1.0-5.0	Mo	233	80.5	8050	<50	<5		
18	1.0-5.0+	Mo	234	0.24	24	<50	<5		
19	2.0-0.0A #1	Mo, U	235	257	25700	42000	4200	46.7	4670
20	2.0-0.0A #2	Mo, U	236	309	30900	49948	4994.8		
21	2.0-0.0A #3	Mo, U	237	362	36200	35200	3520		
22	2.0-1.0	Mo	238	187	18700	<50	<5	3.4	340
23	2.0-2.0	Mo	239	374	37400	<50	<5		
24	2.0-2.5	Mo	240	196	19600	<50	<5		
25	2.0-3.2	Mo	241	406	40600	<50	<5		
26	2.0-5.0	Mo	242	55	5500	<50	<5		
27	2.3-2.5	Mo	243	188	18800	<50	<5		
28	2.9--1.0	Mo	244	1.49	149	<50	<5		
29	3.0-0.0	Mo	245	442	44200	2089	208.9		
30	3.0-2.5	Mo	246	19.6	1960	<50	<5		
31	3.0-3.5	Mo	247	121.5	12150	<50	<5		
32	4.0-0.0	Mo	248	59.4	5940	8323	832.3		
33	4.0-2.5	Mo	249	3	300	83	8.3		
34	4.0-3.5	Mo	250	0.19	19	<50	<5		
35	5.0-0.0	Mo	251	186	18600	13284	1328.4		
36	5.0-2.5	Mo	252	<0.1	<0.5	<50	<5		
37	5.0-3.5	Mo	253	<0.1	<0.5	<50	<5		
38	6.0-0.0	Mo	254	35	3500	223	22.3		
39	6.0-2.5	Mo	255	<0.1	<0.5	<50	<5		
40	6.0-5.0	Mo	256	<0.1	<0.5	<50	<5		
41	7.0-0.0A	Mo	257	<0.1	<0.5	<50	<5		
42	7.0-0.0	Mo	258	<0.1	<0.5	<50	<5		
43	7.0-2.5	Mo	259	<0.1	<0.5	35	3.5		
44	1.0-0.0 S1	Mo, U	260	206	20600	39588	3958.8		
45	2.0-0.0A S1	Mo	261	190	19000	21948	2194.8		
46	4.0-0.0 S1	Mo	262	93.4	9340	28120	2812		

Sample log in and weights

Sample Number	Date Collected	Container Type	Check in Weight (includes container) g	Verticle Distance From Base of Z ft	Horz Distance From Front of ZVI ft	Beta Survey* (by Cotter) dpm	Beta Survey* (by Cotter) dpm	Rad Contamina? (by Cotter) for plot	Bulk Analysis 1 = yes 3 = triplicat	Prime Sample Set 1 = yes	Desciptions
COT-1.0-0.0R	10/28/2004	8 oz Jar	247.9	1.00	0.00	na	na	yes			
COT-1.0-0.5R	10/28/2004	8 oz Jar	155.7	1.00	0.50	na	na	no			
COT-1.0-0.5RA	10/28/2004	8 oz Jar	214.1	1.00	0.50	na	na	no			
COT-1.0-1.0R	10/28/2004	8 oz Jar	249.9	1.00	1.00	na	na	no			Very cemented. Strong
COT-1.0-2.5R	10/28/2004	8 oz Jar	188.2	1.00	2.50	na	na	no			"Fungus" minerals. Bla
COT-2.0-0.0R	10/28/2004	8 oz Jar	221	2.00	0.00	na	na	yes			
COT-2.0-0.0RA	10/28/2004	8 oz Jar	199.5	2.00	0.00	na	na	yes			Front 1" sand zone ah
COT-2.0-2.5R	10/28/2004	8 oz Jar	217.5	2.00	2.50	na	na	no			
COT-2.0-5.0R	10/28/2004	8 oz Jar	168	2.00	5.00	na	na	no			
COT-3.0-0.0R	10/27/2004	8 oz Jar	236.2	3.00	0.00	na	na	yes			From front of PRB.
COT-4.0-0.0R	10/27/2004	8 oz Jar	256.7	4.00	0.00	na	na	yes			From PRB front. Shou
COT-4.0-0.1R	10/27/2004	8 oz Jar	211.3	4.00	0.10	na	na	yes			Same as COT-4.0-0.0
COT-5.0-0.0R	10/27/2004	8 oz Jar	218.4	5.00	0.00	na	na	yes			
COT-5.0-2.5R	10/27/2004	8 oz Jar	227.8	5.00	2.50	na	na	no			
COT-6.0-0.0R	10/27/2004	8 oz Jar	230.9	6.00	0.00	na	na	yes			
COT-7.0-0.0R	10/27/2004	8 oz Jar	216.8	7.00	0.00	na	na	yes			
COT-7.0-0.0RA	10/27/2004	8 oz Jar	223.1	7.00	0.00	na	na	yes			Has greenish material
COT-1.0--0.2	10/28/2004	Bag	680.1	1.00	-0.20	8364	8364	yes			Sand zone. Thick piec
COT-1.0--0.1	10/28/2004	Bag	183.2	1.00	-0.10	17832	17832	yes	1	1	Sand zone. Black. Cer
COT-1.0-0.0	10/28/2004	Bag	1903.6	1.00	0.00	50388	50388	yes	3	1	Large piece of front of
COT-1.0-0.5	10/28/2004	Bag	384.6	1.00	0.50	144.72	144.72	no	1	1	
COT-1.0-0.5A	10/28/2004	Bag	3598.6	1.00	0.50	0	0.1	no			
COT-1.0-1.0	10/28/2004	Bag	801.5	1.00	1.00	120.6	120.6	no	1	1	Very cemented. Strong
COT-1.0-2.5	10/28/2004	Bag	296.8	1.00	2.50	na	na	no	1	1	"Fungus" minerals. Bla
COT-1.0-5.0	10/28/2004	Bag	1054.5	1.00	5.00	-120.6	0.1	no	1	1	"Fungus" minerals. Bla
COT-1.0-5.0+	10/28/2004	Bag	1075.9	1.00	5.10	361.8	361.8	no	1		Downgradient sand zo
COT-2.0-0.0	10/28/2004	Bag	2579.6	2.00	0.00	10920	10920	yes		1	
COT-2.0-0.0A	10/28/2004	Bag	2496.7	2.00	0.00	25620	25620	yes	3		
COT-2.0-1.0	10/28/2004	Bag	218.3	2.00	1.00	252	252	no	1		
COT-2.0-2.0	10/28/2004	Bag	140.6	2.00	2.00	-156.78	0.1	no	1		
COT-2.0-2.5	10/28/2004	Bag	2209	2.00	2.50	-144.72	0.1	no	1		ZVI covered with "fung
COT-2.0-2.5A	10/28/2004	Bag	2891.2	2.00	2.50	48.24	48.24	no			
COT-2.0-3.2	10/28/2004	Bag	373.9	2.00	3.20	na	na	no	1		
COT-2.0-5.0B	10/28/2004	Bag	1511.7	2.00	5.00	373.86	373.86	no			
COT-2.0-5.0	10/27/2004	Bag	589.3	2.00	5.00	494.46	494.46	no	1		Hard ZVI at back of PF
COT-2.0-5.0A	10/28/2004	Bag	898.5	2.00	5.00	554.76	554.76	yes			
COT-2.3-2.5	10/27/2004	Bag	5471.6	2.30	2.50	458.28	458.28	no	1		Large sample for Mo c
COT-2.9--1.0	10/27/2004	Bag	332.5	2.90	-1.00	96.48	96.48	no	1		Upgradient sand zone.
COT-3.0-0.0	10/27/2004	Bag	385	3.00	0.00	1416	1416	yes	1	1	
COT-3.0-2.5	10/27/2004	Bag	418.1	3.00	2.50	-48.24	0.1	no	1		
COT-3.0-3.5	10/27/2004	Bag	400.1	3.00	3.50	192.96	192.96	no	1		
COT-4.0-0.0	10/27/2004	Bag	1357.8	4.00	0.00	31404	31404	yes	1	1	Dry. Fizz with HCl.
COT-4.0-2.5	10/27/2004	Bag	230.5	4.00	2.50	-108.54	0.1	no	1		Dry. Fizz with HCl.
COT-4.0-3.5	10/27/2004	Bag	321.7	4.00	3.50	36.18	36.18	no	1		Dry.
COT-5.0-0.0	10/27/2004	Bag	323.8	5.00	0.00	3936	3936	yes	1		
COT-5.0-2.5	10/27/2004	Bag	505.7	5.00	2.50	-24.12	0.1	no	1		
COT-5.0-3.5	10/27/2004	Bag	595.9	5.00	3.50	241.2	241.2	no	1		
COT-6.0-0.0	10/27/2004	Bag	1016.5	6.00	0.00	720	720	yes	1	1	Fizz with HCl. Charact
COT-6.0-2.5	10/27/2004	Bag	570	6.00	2.50	373.86	373.86	no	1		
COT-6.0-3.5	10/27/2004	Bag	860.4	6.00	3.50	108.54	108.54	no			
COT-6.0-5.0	10/27/2004	Bag	832.8	6.00	5.00	621.09	621.09	yes	1		From contact with san
COT-6.5-0.0	10/12/2004	Bag	140.7	6.50	0.00	1236	1236	yes			
COT-6.9-3.5	10/12/2004	Bag	592.6	6.90	3.50	na	na	na			No fizz with HCl.
COT-7.0-0.0A	10/12/2004	Bag	3054.5	7.00	0.00	1212	1212	yes	1	1	Sample is from front fa
COT-7.0-0.0	10/12/2004	Bag	331.4	7.00	0.00	1464	1464	yes	1		
COT-7.0-2.5	10/27/2004	Bag	1977.6	7.00	2.50	-229.14	0.1	no	1		Sample includes top s
		SUM	47289.8					SUMS	34	11	

* Corrected for background
na = not analyzed
"fungus" grains = white crystals of varied textures ranging from fibers to amygdules. Pervade throughout sample.

From: Sarah Morris
~~ht:~~   Wednesday, October 06, 2004 11:41 AM
                   Stan Morrison; Darlene Depinho; Dave Janssen; Scott Williams; Mark Reed; Thomas Maveal
~~ubject:~~   Sample Shipment from Cotter Mill, Canon City

The following is presented to outline the handling of a shipment of potentially radioactive samples obtained from the PeRT wall at the Cotter Mill, Canon City, CO.

The PeRT Wall at the Cotter Mill in Canon City, CO is scheduled to be sampled the week of 10/11/2004. Samples will be packaged and returned to GJO for analysis in the ESL. Samples will consist of iron filings that have been exposed to uranium-contaminated ground water. There is a possibility that some of the samples will have an elevated rad count. This will be determined by a Cotter Health and Safety tech using a hand-held rad detector. Non-rad samples will be placed in a cooler for non-regulated transport. Those samples with an elevated count will be transported as a hazmat shipment.

The rad samples are of the same type acquired at Monticello last year. Based on the information obtained from the Monticello samples, a worst-case calculation has been made (by S. Morrison). The radionuclides and maximum activity potentially present are:

$$234U = 22 \ Bq/g$$
$$235U = \ 1 \ Bq/g$$
$$238U = 22 \ Bq/g$$

Total activity = 45 Bq/g

Due to the new DOT hazmat regulations, both the activity per sample combined with the probable weight of multiple samples in one package preclude the shipment being unregulated.

~~From~~ 49CFR173.435 the most restrictive A2 value imposed the 3 radionuclides is 6.0×10^{-3} TBq on 234U. The other two unlimited.

To be considered limited quantity, the activity limits for normal form solids is 10^{-3} of the A2 value or 6.0×10^{-6} TBq (49CFR 173.425). This converts to an allowed activity for limited quantity shipment of 6,000,000 Bq. The samples are well under this limit.

SO... The shipment will be classified as Radioactive material, excepted package-limited quantity of material, UN2910 The requirements for this shipment are found in 49CFR173.421 and .422

No shipping papers
No labels
Sample containers must have a rad sticker attached
UN 2910 marked on the outside of the package
Driver must have Hazmat General Awareness and Driver Training

Health and Safety will be notified when the samples arrive at GJO.

Please respond with any comments no later than COB Wednesday, 10/6/2004

1

Logger Pro Uptake Column - Cotten Site

Date/Time	Logger Pro File	Fluid	Logger Pro Elapsed Time	pH in	pH out	ORP in	ORP out	Inlet P (PSI)	Flow set (actual) Rate ml/min	
12/6/04 9:08	DECU6.01	COTTER 1453 SPF	0.0000	na	na	na	na	0.0	4.0	Started pump & logger Pro
9:32	"	"	0.4000	7.43	na	-126.46	na	0.0	4.0	Flow starting to enter column bottom *pH source *ZVI is wet so difficult to = 7.27 tell when enters ZVI
9:38	"	"	0.333	7.42	NA	-98.47	NA	0.0	4.0	Source = pH 7.25
10:21	"	"	1.200	7.43	na	-73.20	NA	0.0	"	Source pH = 7.20. About 1/3 full.
11:15			2.133	7.34	NA	-146.02	NA	0.0	4.0	pouch pH = 7.31 ~80% full
11:45			2.567	7.33	NA	-163.68	NA	0.5	4.0	Source pH = 7.59 @top of solids
11:50			2.667	7.35	NA	-163.41	NA	0.5	4.0	1st outflow start frac collector 34" drain to Colle
11:56			2.800	7.37	9.19	-162.59	NA	0.5	4.0	outflow reaches pH probe
12:21			3.233	7.49	9.87	-173.46	-327.26	0.5	4.0	both outflow probes submerged
12:55			3.800	7.62	9.86	-173.74	-355.79	0.9/1.5	4.0	↑CO₂ to 1 ounits
13:07			3.967	7.66	9.84	-174.82	-345.47	0.9/1.5	4.0	Start tube 2, ATpH = 7.32 ↓CO₂ to 5
14:26			5.300	7.41	9.83	-155.26	-341.39	1.5	4.0 (3.67)	Start tube 4 STpH = 7.13
16:26			7.300	7.47	9.80	-122.11	-320.20	1.5	4.0 (3.67)	Start tube 7 STpH = 7.26
19:40			10.500	7.53	9.70	-77.27	-306.72	1.5	4.0	Between 3-11 and 3-12 STpH = 7.31
2/7/04 06:40			21.500	7.42	9.07	-25.10	-230.53	1.5	4.0	Between 28 and 29, ST pH = 7.16
07:54			22.767	7.40	9.04	-24.01	-225.91	1.5	4.0	start 30 STpH = 7.12
10:34			25.433	7.34	9.00	-20.21	-218.57	1.5	4.0 (3.67)	end 34 STpH = 7.07
14:28			29.333	7.33	8.96	-13.14	-199.55	1.5	4.0 (3.67)	Start 40 STpH = 7.12
15:48			30.667	7.35	8.94	-15.05	-188.41	1.5	4.0 (3.67)	Start 42 STpH = 7.12
15:54			30.767	7.36	8.95	-15.05	-188.68	1.5	4.0 (3.67)	end 42
15:54			30.767	7.36	8.95	-15.05	-188.68	1.5	1	restart flow @ 1 ml/min
19:03			33.900	7.36	8.87	-21.30	-144.39	1.5	1	Δ collect times 136" drain/24" collect
2/8/04 06:30	"	"	45.333	6.68	8.93	26.80	-118.85	1.5	1	between 43/44 pHST = 7.17 Between 47/48 pH ST = 6.10
07:30			46.367	6.59	8.93	45.28	-104.72	1.5	1 (0.92)	Start 48 ST = 7.25 Hg probe replaced
14:11	"	"	53.033	7.13	8.86	-4.72	-100.91	0	1	New P gauge ST = 7.14 between 50/51
16:40			55.567	7.19	8.78	-19.67	-91.13	0	1	Between 51/52 ST = 7.09 90 min left
2/9/04 06:50	"	"	69.700	7.32	8.85	-46.30	-107.	0	1	Between 56/57 ST = 7.10
13:15			76.133	7.31	8.83	-50.64	-114.23	0	1	end 59 ST = 7.08 reset frac collect
1810			81.067	7.30	8.81	-48.74	-123.19	0	1	Start 61 ST = 7.07
2/10/04 07:11			94.033	7.30	8.86	-61.57	-156.89	0	1	Bet. 65/66 ST = 7.08
2/11/04 20:51	"	"		7.21	8.88	-60.70	-210.	0	1	START 80 ST = 6.97
20:56	DECI1-01		0.00	"	"	"	"	0	1	START new log pro file DEC11-01 (500 hours

DATE/Time	LOG-PRO File	Fluid COTTER	LOG PRO Time	pH in	pH out	ORPin	ORPout	Inlet P	Flow set (Actual) RATE (ml/min)	Comments
2/13/04 06:53	DEC11-01	SPF 1455	34.033	7.23	8.93	−68.31	−307.15	0.0	1.0	Between 92/93. ST pH = 7.01 ST sample
2/13/04 17:31	"	"	44.667	7.31	8.91	−74.83	−331.61	0.0	1.0	SYSTEM STOPPED. Shut off frac. coll., pump, and log pro. D/c gasses. LAST Tube = 96
2/16/04 1023	DEC16-01	"	0	7.35	7.78(NA)	122.18	148.26(NA)	~0.5	1.0	(col was shut down 65 HR) Restart. Collect every 24 mins / no drain pHST 6.96
1032	"	"	0.133	7.36	7.77 (NA)	120.27	114.84(NA)	0.75	"	
1232	"	"	2.133	7.36	7.59	117.01	55.06	0.75	"	Collecting 102 pHST = 7.00
1551	"	"	5.467	7.34	8.12	80.87	−13.96	0.75	"(0.92)	Collecting 110 ST = 7.09
1648	"	"	6.400	7.35	8.25	66.74	−32.17	0.76	1.0 "	Restart frac coll start 113 ST = 7.11 Collected ST @ 0647
2/17/04 0632	"	"	20.133	6.96	8.87	−11.24	−173.74	0.75	1.0	pHST = 6.65 Tube 147
0712	"	"	20.833	6.96	8.86	−13.14	−184.33	0.75	1.0	FRAC. COL Reset 136 drain 24 collect. start tube 149
1623	"	"	30.000	7.11	8.20	−26.46	−284.06	0.75	1.0	Between 151/152 62m left pHST = 6.89
1752	"	"	31.467	7.14	8.71	−29.45	−296.29	0.75	1.0 (0.92)	END of Tube 152. pHST = 6.93
2/18/04 12:33	"	"	50.167	7.12	8.78	−49.01	−341.12	0.75	"	END of 159. pHST = 6.79
2/19/04 16:45	"	"	78.367	7.07	8.64	−53.90	−374.81	0.74	1.0 (0.92	Between 169-170 41min left pHST = 6.74
2/20/04 0626	"	"	92.033	7.07	8.68	−60.43	−357.70	0.76	"	174-175 22 min left pHST = 6.74
0649	"	"	92.433	7.06	8.70	−60.70	−360.14	0.76	"	Start 175 pHST = 6.82
1656	"	"	102.533	7.22	8.61	−73.20	−389.76	"	"	Btw. 178/179, 32 min left pHST = 6.91
2/24/04 0625	"	"	116.033	7.20	8.46	−79.45	−383.51	0.75	"	Btw. 183/184 pHST = 6.59
0713	"	"						0.75	"	END Tube 184. Switch to Cotter 1455
0726	Switched to → HIGH pH 1455		117.067	7.20	8.48	−80.26	−388.13	0.75	"	between 184/185 121 min left pHST = 10.18 sample
0862	"	"	119.833	7.92	8.46	−75.10	−389.76	0.75	"	between tube 185/186 116 left pHST = 10.18
1030	"	"	120.133	8.12	8.43	−77.54	−389.76	0.75	"	" 98 left pHST = 10.16
1458	"	"	124.600	9.60	8.46	−104.72	−389.76	0.75	"	Tube 187 filling pHST = 10.14
1823	"	"	128.033	9.91	8.21	−120.21	−389.76	0.75	"	Between 188/189 104" left pHST = 10.12
2/22/04 0630	"	"	140.133	10.26	8.50	−117.76	−389.76	0.75	"	Between 192/193 pHST = 10.11
0636	"	"	140.233	Shut down to cal outflow probes						pH10 = 10.13, ORPbuff = +202.88
0643	DEC22-01	"	0	10.26	8.92	−116.94	106.96	0.75	1.0	Restart. Bt. 192/193 5.2 min left, pHST = 10
1538	"	"	8.900	10.31	8.84	−77.82	−369.11	0.76	"	Betw. 196/197 110 min left pHST = 10.13
1619	"	Low pH 1455	9.600	10.31	8.76	−75.10	−372.37	0.76	"	Switched to Low pH SPF 1455 pHST = 6.94 Bet. 196/197. 69 mins left

ATE/Time	LOG-PRO File	Fluid	LOG-PRO Time	pH in	pH out	ORP in	ORP out	Inlet P (psi)	Flow Set (Actual) Rate mL/min	Comments
2/26/04 0634	DEC22-01	Cotter SPF 1455	95.833	5.95	8.52	116.47	-334.87	0.75	1	pH$_{ST}$ = 5.65. Sampled ST. N$_2$ TANK out B. Tw 228/229
0650	"	"	96.100	5.96	8.57	116.74	-334.33	0.75	1	START TUBE 229
0714	"	"	96.500	5.96	8.65	116.74	-332.70	0.75	1	END 229. Reset F.C. 136 drain 24 collect
0800					Source tank being N$_2$ purged to bring pH up. new N$_2$ TANK (* see notes)				1	Added more fluid to ST (had calcite*)
0958	"	"	98.233	5.97	8.72	117.24	-329.48	0.74	1	Drain b/you 230. pH$_{ST}$ = 6.35
2/27/04 0628	"	"	119.733	7.68	8.80	8.32	-389.76	~0.6	1	Between 237/238 pH$_{ST}$ = 8.13 collected ST
0809	"	"	121.433	7.73	8.81	3.16	-389.76	~0.5	1	Btw 238/239 81min left pH$_{ST}$ = 8.16
0831				Reset FRAC collect. Drain = 34", Collect = 6", Flow RATE to 4mL/min. Switched to Cotter SPF 1453							Fluid w/o U or Mo. 60 min were left on drain between tubes 238/239. pH$_{ST}$ = 10.31 (Bubbling N$_2$)
0911	DEC22-01	Cotter SPF 1453	122.467	8.80	8.79	2.07	-389.76	~0.5	4(3.67)	END TUBE 239. pH$_{ST}$ = 10.30
12:25	"	"	125.700	10.18	8.79	-35.43	-389.76	~0.5	4	START TUBE 244. pH$_{ST}$ = 10.28
13:11	"	"	126.467	10.25	8.97	-44.39	-389.76	~0.5	4	END TUBE 245 pH$_{ST}$ = 10.28 Added fluid to
15:45	"	"	129.033	10.34	9.34	-62.33	-389.76	~0.5	4	Start 249 pH$_{ST}$ = 10.26
17:05	"		130.367	10.33	9.46	-62.06	-389.76	~0.5	4	Start 251 pH$_{ST}$ = 10.27
1/28/04 0632			143.800 143.933	10.28	9.67	-47.93	-378.08	~0.4	4	END TUBE 271 pH$_{ST}$ = 10.19
0636				SHUT DOWN pump to check pHout probe calibration						
06:47			144.067							BACK on line
07:12	"	"	144.467	10.28	9.89	-41.13	-359.87	~0.4	4	END TUBE 272 pH$_{ST}$ = 10.18 Add 2L of 10.75 SPF 1455
07:51			145.133	10.54	9.83	-38.42	-389.76	~0.4	4	end Tube 273 pH$_{ST}$ = 10.64 fresh
12:26	"	"	147.733	10.66	9.85	-48.47	-389.76	~0.4	4	Start Tube 280 pH$_{ST}$ = 10.58
2/29/04 06:33	"	"	167.833	10.67	10.23	-35.97	-389.76	~0.5	4	END TUBE 307 pH$_{ST}$ = 10.56 Added more SPF 1455 0800 - Source sam
~08:00			169.333			Power glitch					
08:11	Dec29.01	1453	0.000			Restart LOG PRO - new file			4	Betw. 309/310 16min left
09:12	"	"	1.033	10.74	10.26	-24.56	-389.76	~0.5	4	end 311 ST pH = 10.65
10:27	"	1455	2.267	10.72	10.28	-19.67	-389.76	~0.5	4	Start 313 *switched to SPF 1455 (fresh batch) pH$_{ST}$ = 6.99
18:20	"	"	10.133	7.36	10.16	95.82	-389.76	~0.5	4	Betw 324/325 7min left pH$_{ST}$ = 7.07
2/30/04 0708	"	"	22.933	7.33	9.19	100.98	-389.76	~0.5	4	Start 344 pH$_{ST}$ = 7.06
08:33	"	"	24.367	7.34	9.13	100.44	-389.76	~0.5	4	end 346 pH$_{ST}$ = 7.06
09:59	"	"	25.700	7.34	9.08	99.89	-389.76	~0.5	4	end 348 pH$_{ST}$ = 7.06
14:20	"	"	30.300	7.34	8.75	95.28	-389.76	~0.5	4	start 355 pH$_{ST}$ = 7.06
14:34			30.367						1	end 355 Drain bflow 356 to 136" Switch to 136 drain 24 collect. Flo
17:15	"	"	33.067	7.35	8.56	94.19	-389.76	~0.5	1	end 356 ST pH = 7.07

Date/Time	Log Pro file	Fluid	Log Pro Time	pHin	pHout	ORPin	ORPout	Inlet P (PSI)	Flow Set (actual) rate ml/min	Comments	
12/31/04 1300	Dec29-01	1455	52.800	7.35	8.01	74.35	-389.76	~5	1 (.92)	Bet 363/364 @ 70min left pHST=7.05	pN₂+ 10% pCO₂+
1/1/05 1300	"	"	76.800	7.34	7.69	57.51	-389.76	~0.5	1	Bet 372/373 @ 71min left pHST=7.03	85% samp ST
1327	"	"/N₂	77.267	Switched to aerated water. +CO₂					1	Bet 372/373 @ 45min left	
1411	"	"/Air	78.000	7.35	7.73	58.59	-389.76	~0.75	1	START TUBE 373	pHST=7.17
1/2/05 1715 ~0930		"	97.433	7.35	7.52	113.75	-389.76	~0.5	1	Bet 380/381 @ 114 left pHST=7.11	sample ST
1715			105.067	7.37	7.42	111.31	389.76	~0.5	1	end 283 pHST=7.16	
1853			106.700	7.38	7.43	109.68	-389.76	~0.5	1	bet 283/284 @ 38 left pHST=7.16	
1/3/05 0747	"	"/Air	119.600	7.37	7.41	104.24	-389.76	0.7	1	bet 388/389 @ 65" left pHST=7.14	collect ST
0805	stopped flow to check cal on out flow probes. Frac Col and LogPro left on (see notes)		119.900									
0830			120.300	Switched back to N₂ purge O/c Air					1	bet 588/389 22" left	
0842	"	1455/N₂	120.533	BACK on line. LOST 40 mL.					1	bet 388/389 9.3" left	
0852	"	"	120.667	7.37	4.53	104.24	-3.63	~0.5	1	START 388.	pHST^N₂=7.05
1436	"	"	126.400	7.30	7.37	34.95	-263.41	0.9	1	END 391	pHST^N₂=6.98
1440	"	"	126.500	Added new 1455 to ST.				0.9	1 (.92)	Bel. 391/392 (32" left pHST^new N₂=7.31	
1452	"	"	128.667	7.31	7.39	71.36	-304.98	0.9	1	START 392, pH^N₂=7.07	collected ST
1/4/05 0612	"	"	142.033	7.34	7.25	46.91	-385.96	0.9	1	Start 397, pH^N₂=7.06	
0636	"	"	142.433	7.34	7.26	47.18	-389.76	0.9	1	END 397, pHST=7.07	
0636 shutdown, 0639 Restart				Increased Flow, Reset Frac coll, 1.2"collect, 10.0" drain						FLOW = 20 ml/min	
0650	"	1455/N₂	142.633	7.36	9.18	49.63	-389.76	0.9	20 (18.333)	Start 398 pHST=7.07	
1023	"	"	146.200	7.39	8.12	65.11	-389.79	0.9	20	Start 417, pHST=7.12	
1515	"	"	151.267	7.36	8.04	70.55	-389.79	0.9	20	Start 444 pHST=7.08	
1708	"	"	152.967	7.39	8.04	70.28	-389.79	0.9	20	END 453 pHST=7.10	
1708	Shut system down. Clamped column off. Shut down Log pro, frac col, pump, N₂, CO₂. Changed P gauge										
1/5/05 0700	JAN05-01	1455/w2kCO₂	0.00	Restart system @ 40 ml/min Collect 0.6". Drain 4".						Start Drain before 454 pHST=7.15	collect ST
0704	"	"	0.067	7.69	7.54	-21.72	-304.72	0.9	40	START 454 pHST=7.13	
0706	Tube was not in ST. Put it in!									START 456 pHST=	
0713	"	"	0.200	7.40	8.25	-1.46	-207.97	1.2	40	START 456 pHST=	
0736	"	"	0.600	7.33	7.65	11.04	-252.27	1.2	40	START 461 pHST=6.99	
0755	"	"	0.900					1.2	40	Start 465 pHST=7.03	
0809	"	"	1.133	7.46	7.37	15.12	-251.45	1.2	40	Start 468 pHST=7.15	
0955	"	"	2.900	7.19	7.74	40.11	-354.44	1.1	40	Start 491 pHST=6.86	
1023	"	"	3.367					1.1	40	Start 497 pHST=7.23	

HE/Time	LOG Pro File	Fluid	LOG Pro Time	pH in	pH out	ORP in	ORP out	Inlet P (psi)	Flow Set (actual) Rate ml/hr	Comments
15/05 10.28	JAN05 01	1455/N₂/CO₂	3.433	7.44	7.26	34.41	-370.47	0.91·1	40 (30...)	new RACK in FRAC col. start 498
1306										Added new fluid to ST
1310 1410	"	"	6.133	7.62	7.92	41.47	-389.76	1.4	40	Start Tube 533 pH_ST = 7.36
1342	"	"	6.700	7.38	7.94	52.61	-389.76	1.1	40	Start 540 pH_ST = 7.08
1348	"	"	6.800						1	AT END of 541, reset Frac. col. 130" dr 24" coll
1751	"	"	10.833	7.32	7.76	68.10	-389.76	1.0	1	Betw. 542/543 53" left pH_ST = 7.00
16/05 0632	"	"	23.533	7.26	7.94	34.14	-389.76	1.0	1	Betw. 547/548 91" left pH_ST = 6.96 ST temp
1324	"	"	30.367	7.29	7.93	33.85	-389.76	1.0	1	START 550 pH_ST = 7.00
1414	SHUT SYSTEM down to CAL. PROBES AND Move outflow probes to outlet area (closer). Be
1414			31.233							Betw. 550/551 110" left
1445	JAN05-02	1455/N₂	0.000	Not to probes yet				0.9	1	Start drain before 551. 130" drain 24" coll pH = 7.0
1643	"	"	1.933	7.28	8.19	115.93	-90.32	0.5	1	Drain before 551 17" left. pH_ST = 7.00
17/05 1445	JAN07-01	"	0.000	7.26	9.06	29.79	-317.75	0.5	1	end 559 pH_ST = 6.9
1944	"	"	4.967	7.29	9.14	29.79	-374.54	0.8	1	during 561 21" left pH ST 7.01
10/05 0646	"	"	64.000	7.23	9.41	24.35	-389.76	1.0	1	END 583 pH_ST = 6.93
11/05 0647	"	"	88.000	7.35	9.39	-6.62	-389.76	1.0	1	END 591 Source Tank > Ampee pH_ST = 7.09
12/05 0647	"	" low N₂	112.800	6.82	9.39	71.91	-389.76	1.0	1	END 601 RAN OUT OF N2 LAST NIGHT pH = 6.23
0722	"	1455/N₂/CO₂	112.600	Started new tank of Argon to ST					1	
13/05 0647	"	"	136.033	7.30	9.43	2.89	-389.76	1.0	1	END 610. pH_ST = 7.04
14/05 1017	"	"	163.533	7.26	9.42	12.40	-389.76	1.0	1	Between 620/621 85" left pH_ST = 6.96 Collect ST
1244	"	"	165.967	Stopped column. Clamped off D/C log pro, frac.col, pump						Drain open 621 99" left.
18/05 0700	Pressure in column = 3.5 psi							3.5 psi	0	
19/05 0621	Pressure " " = 3.9 psi							3.9	0	
20/05 0652	" " " = 4.3 psi							4.3	0	
20/05 1200	JAN20.01	1455/N₂/CO₂	0.00	⊆ Col. was down for 140 hrs				1.1	40	START 622 Restart. Collect 0.6" no drain pH_ST = 6.88
~12" 1226	Shutdown		0.433					1.1	40	Shutdown @ 12:26 end 658
26/05 0658	Pres. = 1.5							1.5	0	
2/3/05 0704	Pres = 2.1							2.1	0	
2/6/05 0725	Pres = 2.5							2.5	0	

Mo Uptake Column - Cotter Site

12/3/04 Placed 2081.9 g* of sample COT-2.3-2.5 (relatively loose ZVI from mid
         portion of the PRB) in a 2" clear acrylic column. This ZVI is wet
         * therefore, we must correct for dry weight. #DRY WEIGHT = $\boxed{1914 g}$

         Placed ~~249.7 g~~ of wet ZVI in aluminum pan. Oven dried at 100°C to get
         242.0 g   moisture content. Net dry 220.7g   LOD = 21.3g 8.8%

17:00 Made about 5 gal of SPF Cotter well 1455

12/6/04 06:35 CALIBRATE probes. File = Dec 06-01. $ORP^{Probe 3}_{zobell} = +188.75$, $ORP^{Probe 4}_{zobell} = 209$

pH Probe	Position	Reading pH 7	Reading pH 10	pH 4	pH 7	pH 10
1	Inlet	1.769	~~0.952 0.979~~	4.05	6.94	9.96
2	Outlet	1.768	0.952	4.12	7.02	9.97

pH 1 = Inlet   ORP 3 = Inlet   pH 2 = OUTLET   ORP 4 = outlet

Source TANK HAS SPF COTTER 1455 with Helium/CO_2 mix bubbling through aeration stone
     (the 2 gasses are mixed together and bubbling from same stone) Will ATTEMPT
     to hold pH at 7.26 (the field pH) using the gas mixture.
     Measured U conc = 1241.3 µg/L
              Mo   = 8.48 mg/L
              alk   = 280 mg/L as $CaCO_3$

Fraction collector programmed for 34" drain / 6" collect   200 ul conc HNO_3 added to each tube

1150 Start fraction collector Cale pv 1 = 506 mL or $\boxed{470 ml}$ -use this
      138" x 3.67 mL/min = 506 mL   or 128" x 3.67 = 470 mL   (visual of liquid @ Top of solids)
                                                                    = 138" - 5" top - 5" bottom = 128"

Mo Uptake Column - Cotter Site

12/6/2004 Reset frac collector to position 1 @ end of tube 7. Combine tubes in groups of 3's for analysis

12/7/2004 Column appears to be running well. Reset frac collector @ end of tube 30. All tubes of sample are clear and contain ~ 22mL. Combine in groups of 3 for analysis.

1100 Source Tank   Mo = 8.24 mg/L   Fe = <0.1 mg/L
                   U = 1351.8 ug/L   Ca = 233 mg/L
                   Alk = 230 mg/L as CaCO₃

prepare addl tubes using 100 µl conc HNO₃ starting tube 1-40

15:54 ↓ flow to 1mL/min, change collection times to 136" drain, 24" collect. One complete cycle (3 drains/ 3 tubes) will take 8 hrs. So 3 samples/day. Rack 23 will last 4.9 days.

12/8/04 06:30 He TANK ran out last night pH₃₇ went to 6.10, pH inlet went to 6.66. Changed out tank w/ N₂ Added a few liters of SPF COTTER 1455

0730 Source tank   Mo = 8.04 mg/L   Fe = 0.03 mg/L
                    U = 1407 ug/L   Ca = 230 mg/L
                    Alk = 235 mg/L as CaCO₃
                    pH = 7.35

1410 Installed new P gauge at inlet

12/9/04 0715 Source tank   pH = 7.10   Fe = 0.04 mg/L
                           alk = 255 mg/L as CaCO₃ Ca = 214 mg/L
                           Mo = 8.28 mg/L   DO = 0.61 mg/L
                           U = 1469.8 ug/L

1315 Reset frac. collector. 1750 Add tubes to fill rack (to 103) put 0.1 mL conc. HNO₃ in each

Mo Uptake Column - Cotter Site

2/13/04 0745 Source Tank   pH = 7.01   Fe = 0.04 mg/L
                               alk 235 mg/L as CaCO$_3$ Ca 233 mg/L
                               Mo = 8.36 mg/L   Cl = 102 mg/L
                               U = 1289 mg/L   NO$_3$ = 5 mg/L
                               DO = N/A   SO$_4$ = 1380 mg/L
                                                  Cl = 102 mg/L

     0904 Made new 20L batch of SPF 1455 (Cotter) from solids. Used MoO$_3$ for Mo.

     1035 Reset frac collector to position 1

     1731 System stopped. Shut off frac collector, pump, CO$_2$ pro. D/C gasses. After
           tube 96 (~ 90 minutes into drain p̄ 96)

12/16/04 Downloaded Dec 11_01
          Check CALIBRATION OF pH/ORP PROBES. The probes have been in-line w/o fluid flowing
   0800   since 12/13/04 (i.e. this check should represent worse-case drift)

                    pH 4   pH 7   pH 10   Zobell
                    Buffer   Buffer   Buffer   mV
          (INLET)
           PROBE 1   4.17   7.05   10.06   PROBE 3 (IN)   +183
 (outlet) PROBE 2   4.17   7.09   10.08   PROBE 4 (OUT) +140   Low! Soaked in 20% HNO$_3$
                  Did not recalibrate
                                                      AFTER SOAKing in 20% HNO$_3$ for several mins
                                                            Zobell
                                                      PROBE 3   +226   } Reinserted probes
                                                      PROBE 4   +235

          Purged line w/ new SPF 1455 soln.

   0950 Called source tank sample   pH = 6.93   U = 1311.0 ug/L Fe = 0.07 mg/L
                                       Alk = 235   DO = 0.65 mg/L   Ca = 198.5 mg/L
                                       Mo = 8.36 mg/L

   1023 Restart Col. at 1 mL/min.

12/17/04 0647   Collected source tank   pH = 7.00 , DO = 0.87 mg/L   Alk = 250 mg/L
                                           Ca = 204 mg/L Fe = 0.00 mg/L (<0.1)
                                           Mo = 8.32 mg/L U = 1298.5 µg/L

12/20/04 0850   Collected source tank   pH = 6.94   DO = 0.56 mg/L   alk = 240 mg/L
                                           Ca = 205 mg/L   Fe = <0.1 mg/L SO_4 = 1357 mg/L
                                           Mo = 8.20 mg/L   U = 1340 µg/L   Cl = 100 mg/L

12/20/04 Made a batch of Cotter SPF 1455 @ pH ~10. Made about 2L
          See next page for details. This SPF has Mo and U.

Cotter Column

	1	2	3	4	5	6	7	8	9	10	11	12	13
12/20/04	Titration	of 2L	of Cotter SPF 1455 to Bring pH to 10 or so									
Time ~16:10	Strength NaOH	Amount Added	pH	PPT?									
		0	7.54	No									
	1 N	0.25mL	7.76	No									
	"	0.25	8.02	No									
	10 N	0.25	8.96	No									
	"	"	9.38	? slightly cloudy									
	"	"	9.70	?									
16:25	"	"	10.06	cloudy (yes)									
16:30	0	0	9.63	V. cloudy									
16:31	—	—	9.58	"									
16:31	10 N	0.25	10.27	"									
16:38	—	—	10.23	"									
16:58	—	—	10.17	"	Shut stir bar off								
12/21/04 0632	—	—	9.50	"	Settled out. Filtered through 0.45 um. >95% Recovered								
0648	—	—	9.92	Clear	After filtering								
0654	—	—	9.94	"									
0656	1 N	100 uL	9.97	"									
0657	1 N	0.25mL	10.08	"									
0703	—	—	10.10	"									

12/21/04 0726   Switched inlet tube to Cotter SPF 1455 pH~10.
Purging w/ N₂
between tubes 184 and 185. Sample will be 184-186 when ST changed

0730   Collected ST sample   pH = 10.18   DO NA   alk 90mg/L
                            Ca = 12.1 mg/L   Fe = <0.1 mg/L
                            Mo = 8.16 mg/L   U = 1126.3 ug/L

12/26/04 0634 SOURCE TANK
pH = 5.63
AlK = 220
Ca = 206.5 mg/L
Fe = 50mg/L
< 0.1

Mo = 8.28 mg/L
U = 1314 ug/L
DO = 2.70 mg/L

0800 Added more fluid 1455 to source tank. There was white powder in bottom of carboy (calcite?). I got out most of it. Should go back into solution with CO_2 flux.
CALibrated ST pH probe.
The column is still "pitch" black. No obvious ferric oxide formation.

12/27/04 0628 Collected source tank
pH = 8.13
AlK = 110 mg/L CaCO₃ → AlK = 110 mg/L $CaCO_3$
Ca = 151.0 mg/L
Fe = 50mg/L
< 0.1

Mo = 8.32 mg/L
U = 1205 ug/L
DO = 0.67 mg/L
SO_4 = 1379 mg/L

Cl = 99.5 mg/L

0730 Made 2 L of Cotter SPF 1453 (ZVI zone) 5/25/04 : No U or Mo
NaOH added   pH

Time	Normality		pH	Time	Normality	Amount	pH		TOTALS
		0	8.49	Time	Normality	Amount	pH		
0723	1 N	50 uL	8.62	0730	10 N	100 uL	10.24		
	1 N	100 uL	8.75	0731	10 N	100 uL	10.40		
	10 N	50 uL	9.15	0733	—	—	10.41		
0726	10 N	50 uL	9.37	0745	—	—	10.42		
	10 N	50 uL	9.53	0758	—	—	10.43		
	10 N	50 uL	9.65	0806	—	—	10.43		
	10 N	50 uL	9.77						
	10 N	50 uL	9.87						
	10 N	100 uL	10.05						

0816 collected source tank (1453)
pH = 10.26
AlK = 215
Ca = 0.94 mg/L
Fe = 50 mg/L
< 0.1

Mo = < 0.06 mg/L   DO = NM
U = 0.6 ug/L

12/28/04 0636   Buffer 10 = 10.23 pH.   Buffer 7 = 7.21
            ↳ Shut down pump to check pH/out calibration. Did not turn off frac. coll or log pro
        0647 Back on line. 11 mins not pumped. Drain between 271 and 272 has 23 mins × 3.67 = 84mL

        0700   Made new 2L batch of SPF 1453 (no Mo, no U) at higher pH = 10.75

    0845   Sample ST   pH = 10.63   Ca = 0.96 mg/L   Mo = <0.06 mg/L DO = N/M
                        Alk = 230   Fe = <0.1 mg/L   U = <0.02 ug/L
                        SO₄ = 475   Cl = 96.1 mg/L

12/29/04 0745 Made fresh 20L batch of SPF 1455 ; pH (unadjusted) = 7.69
        0800   Collected ST (1453)
                    pH = 10.65   Fe = 0.01 mg/L   DO = NA
                    Alk = 254   Mo = <0.06 mg/L
                    Ca = 0.47 mg/L   U = <0.02 ug/L

    12/29/04 10:30   Sampled Source Tank (new batch of 1455)
                    pH = 7.01   Fe = 0.02 mg/L   DO = 3.6 mg/L ⟵ not completely purged yet
                    Alk = 250   Mo = 5.56 mg/L   increased purge
                    Ca = 228 mg/L   U = 1264 ug/L

            12:27 ST Ca = 229 mg/L
                    Fe = 0.02 mg/L
                    U = 1272 ug/L
                    Mo = 5.76 mg/L

    12/30/04 0700   Sampled Source Tank (1455)
                    pH = 7.06   Mo = 6.84 mg/L   Cl = 101 mg/L
                    Alk = 246 mg/L CaCO₃ U = 1315.3 ug/L   SO₄ = 1382 mg/L
                    Ca = 197 mg/L   DO = 0.44 mg/L
                    Fe = 0.02 mg/L

1/1/05   ST sample 1455 N_2 purge.
1300   pH = 7.03   Mo = 6.84 mg/L   Ca = 230 mg/L
           DO = 0.55 mg/L   U = 1255.8 ug/L   Cl = 99 mg/L
           Alk = 220 mg/L CaCO₃   Fe = 0.02 mg/L   SO₄ = 1355 mg/L

1327 Switched to aerated water. D/c N_2, connected aquarium pump. Adjusted CO_2
1355 DO_{ST} = 9.8 mg/L

1/2/05 0940 ST sample 1455   air purge
           pH = 7.11   Mo = 7.24 mg/L   Ca = 230 mg/L
           Do = 7.57 mg/L   U = 1247.3 ug/L   Cl = 99 mg/L
           alk = 240 mg/L CaCO₃   Fe = 0.02 mg/L   SO₄ = 1355 mg/L

1/3/05 0747 ST 1455, Air purge
           pH = 7.14   Mo = 7.2 mg/L   Ca = 231 mg/L
           DO = 8 mg/L   U = 1241.3 ug/L   Cl = 101 mg/L
           AlK = 235 mg/L CaCO₃   Fe = 0.01 mg/L   SO₄ = 1386 mg/L
0800 Made new 20L Batch of SPF 1455 using liquid Mo
     0805 Stopped Flow to check cal. 46" left on drum betw. 385/389. Los Pro @ 114-900
     pH_7^{out} = 7.30   , pH_4^{out} = 4.38   , pH_{10}^{out} = 10.20 ORP_{Zobell}^{out} = 196 mV

     0818 Soaked probes in 20% HNO_3
     AFTER HNO_3 cleaning: pH_4^{out} = pH_7^{out} = pH_{10}^{out} = ORP_{Zobell}^{out} =

          LOST : 37 min @ 0.92 mL/min = 34 mL   + 5 mL spillage from pH = [40 mL LOST]
                                                        probe port

          0842 Back on line
1/4/05 0612 Source tank
           pH = 7.06   Ca = 232 mg/L   Mo = 7.88 mg/L
           Alk = 246 mg/L CaCO₃   Cl = 97 mg/L   U = 1328.0 ug/L
           DO =   SO₄ = 1320 mg/L Fe = 0.01 mg/L

1/5/05   0642   Added new fluid to ST. Purging. Col. still off.
          0700   Collected ST (1455/N2/CO2)

              pH = 7.08   Ca = 234 mg/L   DO = 0.51 mg/L
              AlK = 230 mg/L CaCO₃ Fe = <0.01 mg/L
              U = 1291.0 ug/L   SO₄ = 1257 mg/L
              Mo = 8.4 mg/L   Cl = 95 mg/L

1/6/05 0632   Source TANK
              pH = 7.14   Ca = 235 mg/L   DO = 0.38 mg/L
              AlK = 245 mg/L CaCO₃ Fe = <0.01 mg/L
              U = 1367.8 ug/L   SO₄ = 1309 mg/L
              Mo = 7.76 mg/L   Cl = 98 mg/L

1420   PROBE check
              PROBE #1 pH_7 = 7.22 pH_{10} = 10.19
              PROBE #2 pH_7 = 7.20 pH_{10} = 10.16

              PROBE #3 ORP_{ZoBell} = 179.24

              PROBE #4 ORP_{ZoBell} = 192.01

          SOAKED probes in 20% HNO₃ & AFTER HNO₃ SOAK →

              PROBE #1 pH_7 = 7.01 pH_{10} = 10.03
              PROBE #2 pH_7 = 7.00 pH_{10} = 10.02

              PROBE #3 ORP^{ZoBell} = 201.25
              PROBE #4 ORP^{ZoBell} = 200.71

1/7/05 13:47   Source Tank
              pH = 6.94   Ca = 222 mg/L   Do = 0.35 mg/L
              alk = 215 mg/L CaCO₃   Fe = 0.02 mg/L
              U = 1318 mg/L   SO₄ = 1343 mg/L
              Mo = 7.76 mg/L   Cl = 99 mg/L

     log profile Jan 07-01 @ 500 hrs.   (log pro had D/c'd collection @ 24 hrs on Jan 05-02) Start
     new file @ 14:45

1/10/05 07:58   Source Tank
              pH = 7.07   Ca = 222 mg/L   Do = 0.45 mg/L
              alk = 225 mg/L CaCO₃   Fe = 0.01 mg/L
              U = 1309 ug/L   SO₄ = 1348 mg/L
              Mo 7.44 mg/L   Cl   = 99 mg/L

1/11/05 06:47   Source Tank
              pH = 7.07   Ca = 213 mg/L   DO = 0.50 mg/L
              *AlK = 378 mg/L CaCO₃   Fe = 0.02 mg/L
              U = 1236.8 ug/L   SO₄ = 1169 mg/L
              Mo = 7.52 mg/L   Cl = 86 mg/L

   * AlK measured w/ new 0.16 N H₂SO₄ cartridge. Alk w/ old 1.6 N H₂SO₄ gave 260 mg/L CaCO₃.
          Alk w/ new 1.6 N H₂SO₄ cartridge gave 373 mg/L CaCO₃.
        Conclude that old 1.6 N H₂SO₄ cartridge was bad. ALL previous results
          should be corrected by multiplying by $\frac{378}{260}$ = 1.4538

1/12/05   0647   Source Tank
                    pH = 6.39   Ca = 222 mg/L   DO = 1.26 mg/L
                    Alk = 386 mg/L CaCO₃   Fe = 0.01 mg/L
                    U = 1228.3   SO₄ = 1218 mg/L
                    Mo = 7.76 mg/L   Cl = 91 mg/L

1/13/05   0647   Source TANK
                    pH = 6.99   Ca = 220 mg/L   DO = 0.41 mg/L
                    Alk = 367 mg/L CaCO₃   Fe = 0.02 mg/L
                    U = 1294.5 ug/L   SO₄ = 1243 mg/L
                    Mo = 9.16 mg/L   Cl = 91 mg/L

1/13/05   1057   Began collecting sample for BART test. Collecting directly from drip fitting
         (off frac. collector) into BART sterile bottle. 1mL/min. Will also sample source tank

    1/13/05 12:00   Effluent   } From drain between 611 and 612   1/14/05 10:40   EFF.   ST
    1/13/05 11:00   Source Tank   }   Top of bed   Top of bed
                                                                                               black   black

1/14/05   10:17   Source TANK
                    pH = 6.95   Ca = 219 mg/L   DO = 0.52 mg/L
                    Alk = 365 mg/L CaCO₃   Fe = 0.02 mg/L
                    U = 1316.5 ug/L   SO₄ = 1245 mg/L
                    Mo = 8.96   Cl = 91 mg/L

1/20/05   09:50   Source Tank   pH = 6.88   Ca = 220 mg/L   DO = 0.39 mg/L
                                    Alk = 357 mg/L CaCO₃ Fe = 0.02 mg/L
                                    U = 1364.2 ug/L   SO₄ = 1255 mg/L
                                    Mo = 9.40   Cl = 93 mg/L

1/20/05 11:40   CALIBRATED all pH proBes. check ORP: ORP1 ZoBell = 179 mV   ORP2 ZoBell = 198 mV

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	Well 1455, Upgradient of PRB, 5/25/04 Sample		Solids													
2		mL per	mg per													
3		L of	L of	Na	K	Ca	Mg	NH4	SO4	Cl	NO3	C	Mo	U	Comments	
4		Soln	Soln	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L		
5	Liquid Components															
6	V2O5, V=998mg/L, 2%HNO3	0.00									0.00					
7	V2O5, V=1000mg/L, 5%HNO3	0.00									0.00					
8	V2O5, V=1000mg/L, 1.4%HNO3	0.00									0.00					
9	V2O5, V=1000mg/L, 2%HNO3	0.00									0.00					
10	Na2MoO4.2H2O, Mo=925mg/L	0.00		0.00									0.00			
11	Na2MoO4.2H2O, Mo=1000 mg/L,	0.00		0.00									0.00			
12	(NH4)2MoO4, 1006 mg/L Mo	8.00						3.02					8.05		*U and Mo were increa	
13	U3O8, U=10000mg/L, 3.5%HNO3	0.14									4.74			1.40	the values used in the	
14	U3O8, U=10000mg/L, 5.2%HNO3	0.00									0.00			0.00	Roman Pyrih study.	
15	U Std, U=1000mg/L, 2% HNO3	0.00									0.00			0.00	Also to help with det. l	
16	Ra Std, Ra=68.7pCi/mL, 2% HNO3	0.00									0.00					
17	As Std, As=999mg/L, 5%HNO3	0.00									0:00					
18	As Std, As=1000mg/L, 1.4%HNO3	0.00									0.00					
19	Se =999 mg/L 5% HNO3	0.00									0.00					
20	Cd Std = 1000mg/L, ~2% HNO3	0.00									0.00					
21																
22	100g/L K2CO3	0.00	0.00		0.00							0.00				
23	50g/L NaHCO3	13.70	685.00	187.56								97.86				
24	100g/L Na2SO4.10H2O	8.50	850.00	121.43					253.42							
25	100g/L Na2SO4.(0.89 H2O)	0.00	0.00	0.00					0.00							
26	500g/L (NH4)2SO4	0.00	0.00					0.00	0.00							
27	1.5g/L CaSO4.2H2O	715.00	1072.50			249.80			598.33							
28	1.2 g/L CaSO4	0.00	0.00			0.00			0.00							
29	200g/L MgSO4.7H2O	4.50	900.00				88.79		350.79							
30	100g/L K2SO4	0.10	10.00		4.49				5.51							
31	conc H2SO4(36N)	0.00							0.00							
32	927.2 g/L CaCl2.2H2O	0.00	0.00			0.00				0.00						
33	92.72 g/L CaCl2.2H2O	0.00	0.00			0.00				0.00						
34	300g/L NaCl	0.53	159.00	62.51						96.49						
35	100g/L MgCl2.6H2O	0.00	0.00				0.00			0.00						
36	100g/L NH4Cl	0.00	0.00					0.00		0.00						
37	100g/L NaNO3	0.00	0.00	0.00							0.00					
38	2% HNO3	0.00									0.00					
39	mL 1N NaOH needed to neutralize	0.00		0.00												
40	66.67 g/L NaN3	0.00	0.00	0.00												
41																
42																
43																
44	Totals (mg/L)	750.47		371.50	4.49	249.80	88.79	3.02	1208.05	96.49	4.74	97.86	8.05	1.40		
45	ACTUAL (mg/L)			370.00	4.50	250.00	87.00	?	1400.00	96.00	?	98.00	1.9*	1*		

COT-1.0-0.5 Large chunk vacuum dried

11/3/09   COT-1.0-2.5 R   VAC. Dried. Loose grains. Some hardened into a chunk during drying

COT-1.0-5.0   VAC DRied.

11/5/09   14:49 Placed small chunk of COT-1.0-0.0R (vac. dried) in Lime away

17:27 Rinsed w/ DI 3 times. VAC. DRied for SEM → COT-1.0-0.OR S Z

w/snowball Xtals

17:55 Placed small piece of COT-1.0-0.0R in 10% HCl, The acid bubbled furiously and gradually, all the ZVI grains split apart.

H₂S odor. Snowballs gone after HCl treatment (dissolved?).

11/8/09   15:40 Place a small "chunk" of COT-1.0-0.5A in each of 5 containers. Added liquid (unmeasured) to each. About 30-40 mL.

OBservAtions:

Beaker	Solvent	
1	DI	
2	10% Lime Away	foamed on first addition
3	10% HCl	Moderate bubbling on first addition.
4	Acetone	
5	10% HNO₃	Vigorous bubbling on first addition. Died off in 5 min.

Sample COT-1.0-0.5A viewed under Binoc scope. Sample is full of "snowball" crystal "fungus" mineralization. The outer (<1mm) of the surface has oxidized to red-orange. Interior is still pitch black.

misc-01-15-02

15:57 Sample soaked in DI. (all samples were rinsed in DI prior to observations)
No breakdown of matrix. Many "snowball" and "can" xtals.
Surface is much cleaner that original. May be useful to wash
it prior to SEM look

16:03 Lime-Away soaked sample. Possibly some disaggregation. "Soot" came off w/
repeated washings. Even w/ this brief etching period, there is clearly a
removal of matrix. Individual ZVI shards stand out from surface.
and are "clean" and shiny. Snowball crystals reduced or
gone.

16:10 HCl soaking sample: sulfurous odor. Some breakdown of matrix is apparent.
Matrix largely destroyed. ZVI grains look shiny, almost like originally.
White crystals completely gone.

16:21 Acetone soaked. Appears to be no change. Still many snowballs

16:30 HNO₃ sample. Appears to have disaggregated some of the sample. Still a chunk
however. ZVI grains stand out (like HCl) but not as clean as HCl

1651 DI w/ 30m of sonication in small bath. Some sooty material was removed.
Still chunk however. Surfaces still very "sooty" and many snowballs

11/11/02

Placed a chunk of COT-?.0-0.5A in ~100mL glass jars (3). Added Lime Away to one, 10% HCl to one, and 0.1m Di Na (pH 5) EDTA to one. Replaced fluid twice over 2-day period for good etch.

The HCl nearly completely disaggregated the chunk and the ZVI surfaces are clean and fresh. "Soot" came off when I rinsed it. The "soot" (at high mag) appears to be iron oxide (little or no ZVI as determined with magnet).

The Lime Away etched the chunk quite well and removed visible calcite. Moderate disaggregation. Not nearly as effective as the HCl.

EDTA fails to remove even all the visible calcite, water was red (others were black). It did however, clean off some ZVI grains. So may be worth trying at higher strength or a different EDTA.

February 11, 2005

E-mail and Mail Delivery

Dr. Stan J. Morrison
SM Stoller Corporation
2597 B ¾ Road
Grand Junction, CO 81503

Subject: Microprobe Analysis of Sections of Permeable Zero-Valent Iron Groundwater Barrier
              Hazen Project 10200

Dear Stan:

On November 11, 2004, SM Stoller Corporation authorized Hazen Research, Inc. to characterize insoluble deposits on zero-valent (metallic) iron barrier materials with emphasis on the mode of occurrence of molybdenum, uranium, calcium, iron, and sulfur. The zero-valent iron barrier material provides a reducing environment, resulting in precipitation of the detrimental elements. The objective of this investigation was to assess the effectiveness and limitations of capturing these elements in groundwater. The methodology for the determination was essentially the same as that used in a previous investigation conducted on behalf of Stoller, which consisted of electron microprobe analysis of polished sections of the barrier material. The current work was carried out under Stoller's P.O. #2051 dated November 10, 2004.

Six samples were received at Hazen on November 16, 2004, representing cross sections of the barrier wall at various positions. Table 1 lists the identification and figures (enclosed) for each sample.

Table 1. Samples

Sample	Figure
COT–1–0.5 EM	1 and 2
COT–1–0 EM	3–13
COT–1–5 EM	14–23
COT–1–0.5 HCl EM	24 and 25
COT–1–2.5 EM	26–28
PEER EM	29

Samples COT-1-0.5 EM, COT-1-0 EM, and COT-1-5 EM were received in plastic bottles and Samples COT-1-0.5 HCl EM, COT-1-2.5 EM, and PEER EM were in glass vials. They were stored in a desiccator filled with N_2 prior to polished section preparation. Portions were removed and embedded in epoxy, cut with a saw, and polished. Some of the samples consisted of loose metal shavings; others

consisted of consolidated masses of metal shavings.

Initial microscopic examinations of the polished sections showed layers of variable thickness and generally low reflectivity surrounding the metallic iron particles. From textural relationships, the layers appear to have formed at the expense of the metallic iron and have the optical characteristics of hydrated iron oxides, and in essence represent rust. In the consolidated specimens, the rust has cemented the iron shavings together to form the lumps. The hydrated iron oxide layers are frequently coated by carbonates occurring as crystalline crusts often consisting of radiating crystals. Within the oxide layers and also at the peripheries, thin wavy bands of higher reflectivity that resemble iron sulfide are discernable.

The ensuing electron microprobe analyses revealed that the detrimental elements are invariably associated with the oxide layers and occur in local, fairly high, spotty concentrations or in thin wavy bands that are often at the periphery of the oxide layers. The metal shavings themselves show only iron with low levels of silica and discrete stringers of carbon, probably graphite. It would appear that, with increasing thickness of the oxide layer and deposition of carbonates at the outer edge, the reducing capacity of the metallic iron would diminish over time.

Samples COT-1-0 EM and COT-1-0.5 EM were examined briefly with the microprobe during your visit on December 15, 2004. Rims of hydrated iron oxides containing high concentrations of uranium and occurrences of molybdenum and sulfide were observed in COT-1-0 EM.

The figures in this report are backscattered electron images of the iron oxide layers, with the exception of Figure 25, which is a secondary electron image. Backscattered electron images are better at showing differences in composition based on differences in the average atomic weight of the various phases present in the sample. Bright areas in the images indicate relatively high atomic weight areas, and dim areas show relatively low atomic weight areas. In some of the samples, there are relatively dark coatings for which the elemental analyses total only about 30%, most of which is iron. These areas often appear porous, which would contribute to low totals, but they may also contain carbon, which cannot be detected with the microprobe. Water of hydration may also contribute. Another potential problem affecting the analysis of some areas is the fine-grained heterogeneous mixtures of particles too small to be analyzed individually. These factors make it difficult to specifically characterize many of the iron species that are present. High concentrations of sulfur are often present with the iron in the coatings, and very little oxygen could be detected. The x-rays of oxide sulfur and sulfide sulfur have slightly different energies, providing a means of distinction. Only sulfide sulfur was detected in the samples.

Uranium was detected only in sample COT-1-0 EM, and the highest concentrations of molybdenum were also in that sample. Sample COT-1-0.5 EM had some areas with significant molybdenum concentrations. The highest concentrations of uranium and molybdenum usually occurred together and in combination with iron and sulfur, but it was not possible to identify a uranium or molybdenum compound. There were a few instances in which the sulfur level was low in the presence of high uranium concentrations.

In the enclosed figures, analyses correspond to lettered areas in the photographs. Pertinent observations are provided in the comments for each figure.

If there are any questions regarding this report, please contact us.

Sincerely,

Robert K. Johnson
Metallurgist

Roland Schmidt
Director, Mineralogical Laboratories

RKJ/RS/wcf

Enclosures

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White Bar = 100 μm   200 ×
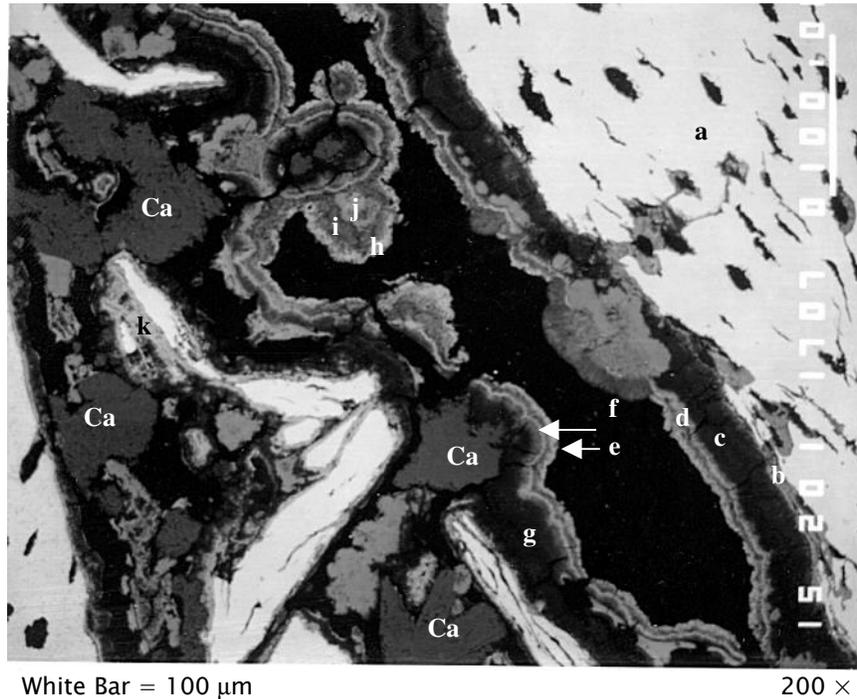
Figure 1. Sample COT-1-0.5 EM, Example 1

Spot	Weight, %				Description
	Mo	Fe	S	Si	
a		96		2.3	Fe Metal
b	0.57	61	0.47	1.4	
c	0.24	21	3.9	2.6	
d		60	19	0.3	Fe Sulfide Rim
e		60	19	0.04	Fe Sulfide Rim
f	0.15	50	2.8	0.9	FeOx (hydrate)
g	0.19	24	4.5	1.6	
h		59	20	0.04	Fe Sulfide Rim
i		41	14	0.1	
j		49	14		
k		68		2.3	
Ca					CaCO₃

The metallic iron (white) is often coated with a dark layer (c and g) containing about 20 to 25% Fe and 4% S, and a lighter outer rim (d, e, and h) with 60% Fe and 20% S. The dark inner layer usually has about 0.2% Mo. In one area (b), the iron oxide layer next to the metal has a relatively high amount of molybdenum. The sulfur is present as a sulfide in all cases. The atomic ratio of Fe/S in the lighter rims is about 1.8:1
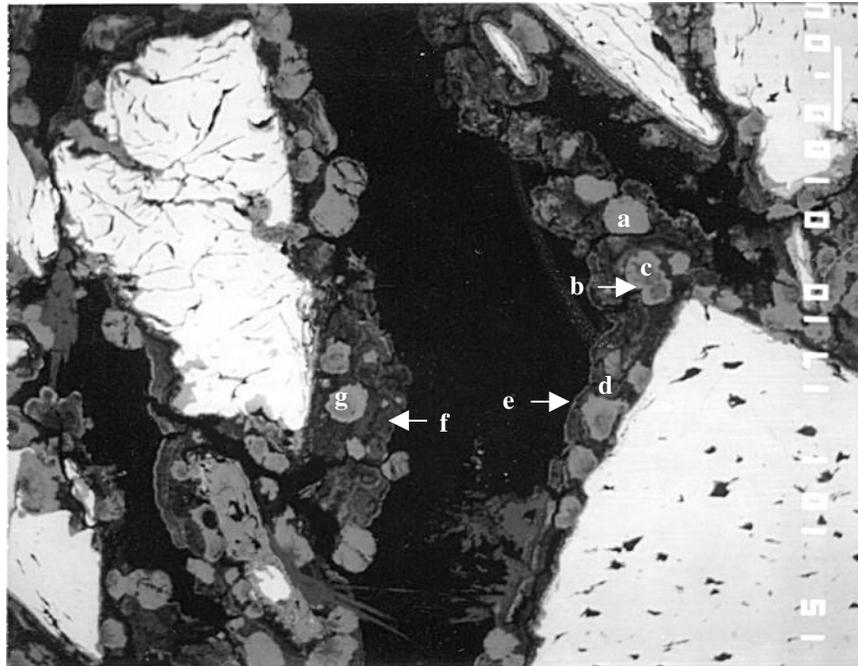
White Bar = 100 µm   100 ×

Figure 2. Sample COT-1-0.5 EM, Example 2

Spot	Weight, %				Description
	Mo	Fe	S	Si	
a	<0.05	57	<0.05		
b	0.06	53	0.1		
c	0.24	53	0.2	0.9	
d		33	12	0.8	Dark Area
e	<0.05	42	14		Light Area
f	<0.05	39	14	1.2	
g	0.25	55	0.12		

The dark layer on the metallic iron (white) contains about 40% Fe and 14% S (as sulfide), but no molybdenum was detected in these areas. Areas a, b, c, and g possibly consist of iron carbonate or iron carbonate-hydroxide.

Hazen Research, Inc.
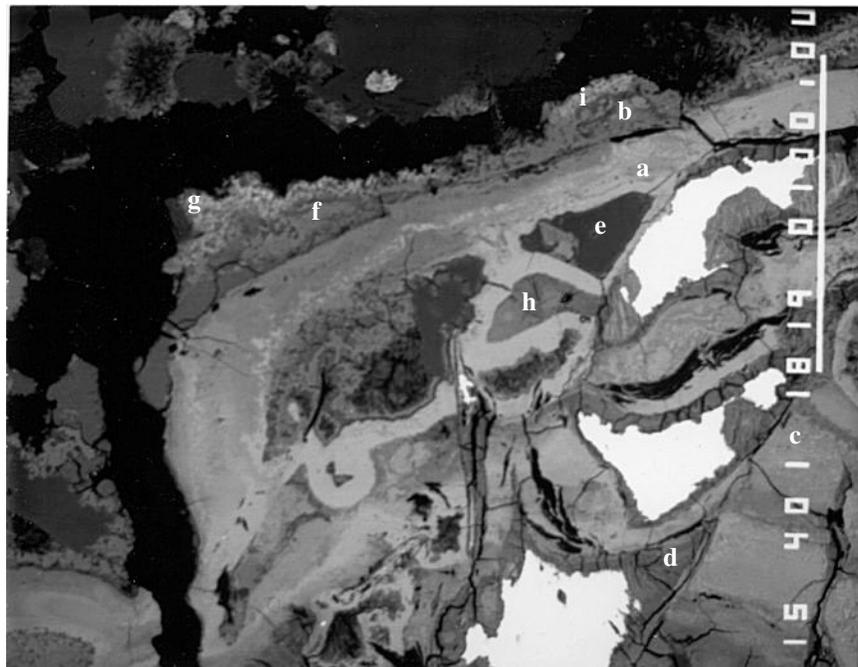
White Bar = 100 µm   400 ×

Figure 3. COT-1-0 EM, Example 1

Spot	Weight, %				Description
	Mo	**Fe**	**S**	**Si**	
a		67		0.9	FeOx (Hydrate)
b		61	0.06	0.4	FeOx (Hydrate)
c		64	0.08	1.5	
d		58	0.13	0.11	
e					CaCO$_3$
f	0.2	47	8	11	
g	3.5	49	20		
h		55	0.1	2.7	
i	2.2	52	22	1.2	Lighter Edge

The molybdenum occurs in the lighter edge (g and i) along with high sulfide sulfur.
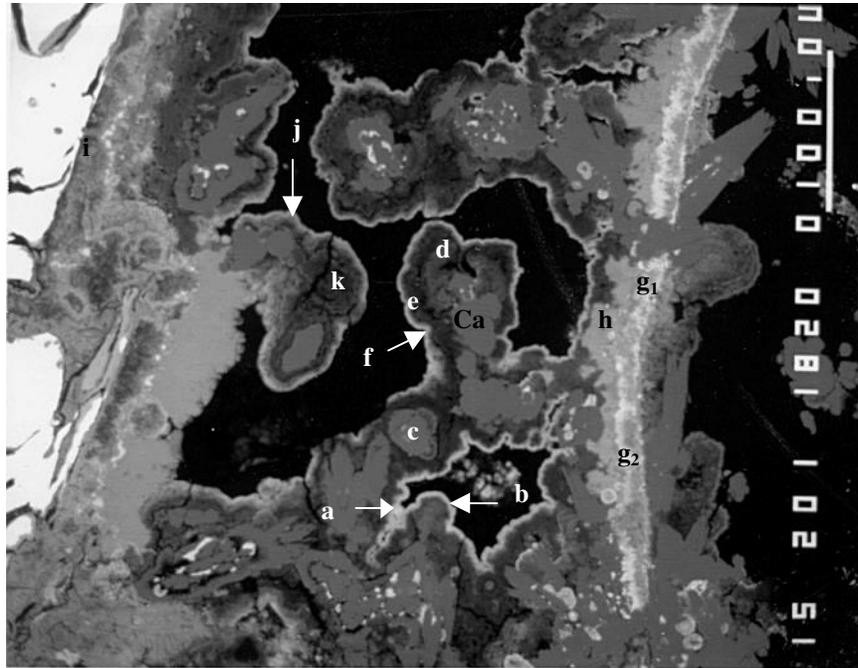
White Bar = 100 μm   200 ×

Figure 4. COT-1-0 EM, Example 2

Spot	Weight, %					Description
	U	Mo	Fe	S	Si	
a		0.31	59	14	0.7	
b		0.34	57	16	0.6	White Rim
c		0.35	20	5.5	1.6	
d		0.66	43	14	1.1	Inner Light Gray Area
e		0.31	29	8	1.0	Dark Area
f		0.23	54	13		
g_1	0.23	0.35	56	27		White Band
g_2	0.12	0.59	60	26		White Band
h		0.33	52	2.4	0.2	
i			54	0.2	1.8	
j		0.22	44	12	0.4	
k		0.26	20	7.9	0.9	
Ca						$CaCO_3$

Uranium was detected only in the white band at the right (spots g_1 and g_2) that has the highest concentration of sulfide sulfur.
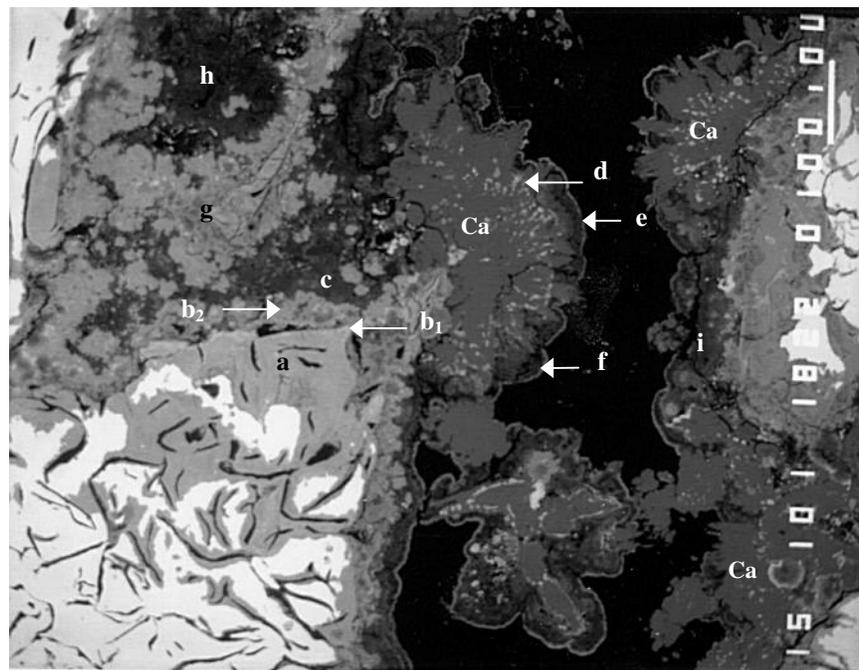
White Bar = 100 μm   100 ×

Figure 5. COT-1-0 EM, Example 3

Spot	Weight, %						Description
	Ca	U	Mo	Fe	S	Si	
a			0.48	64	0.6	4.2	Probably FeOx (Hydrate)
b₁	1.1	1.0	6.4	52	6	4.8	Slightly Lighter Edge
b₂	1.4	0.27	6.5	58	6	3.4	
c	0.14	<.05	1.1	32	13	1.0	
d	1.5	0.07	0.43	56	29	1.6	White Spots
e	0.16	0.07	0.35	41	8	2.8	Darker Zone
f			0.12	50	12	0.6	Lighter Rim
g	0.79	0.07	6.3	58	8	1.7	Lighter Material
h	0.1		1.0	27	12	0.8	
i	0.2	0.12	0.72	33	14	1.0	
Ca							CaCO₃

White Bar = 100 µm   60 ×

Figure 6. COT-1-0 EM, Example 4

Spot	Weight, %						Description
	Ca	U	Mo	Fe	S	Si	
a		5.7	0.31	48	20	3.3	White Rim
b				88		2.1	Metallic Iron
c				90		2.6	Metallic Iron
d			0.28	55	0.74	4.6	
e			0.09	58	0.5		
f			0.16	63	0.7		Lighter Area
g	1.1	0.23	0.47	54	25		White Rim on CaCO$_3$
h			0.05	65	0.05	1.3	
i			1.78	50	20	4.6	
j							Shown Enlarged in Figure 7
Ca							CaCO$_3$
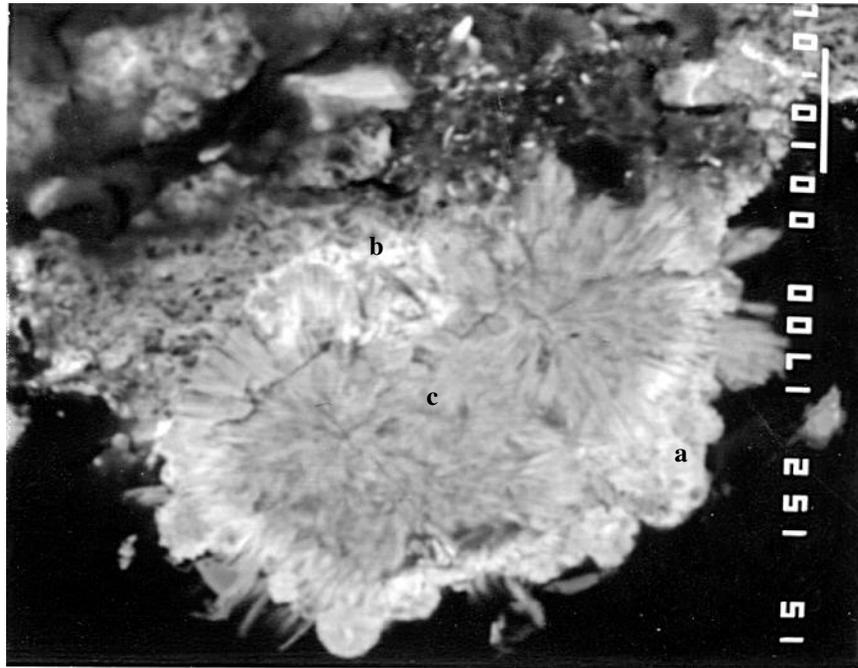
White Bar = 10 μm   1,500 ×

Figure 7. COT–1–0 EM, Enlargement of Area J in Figure 6

Spot	Weight, %						Description
	Ca	U	Mo	Fe	S	Si	
a		11.4	0.24	46	0.6	0.9	
b		14.4	1.00	33	9.8	1.7	
c				55		1.6	
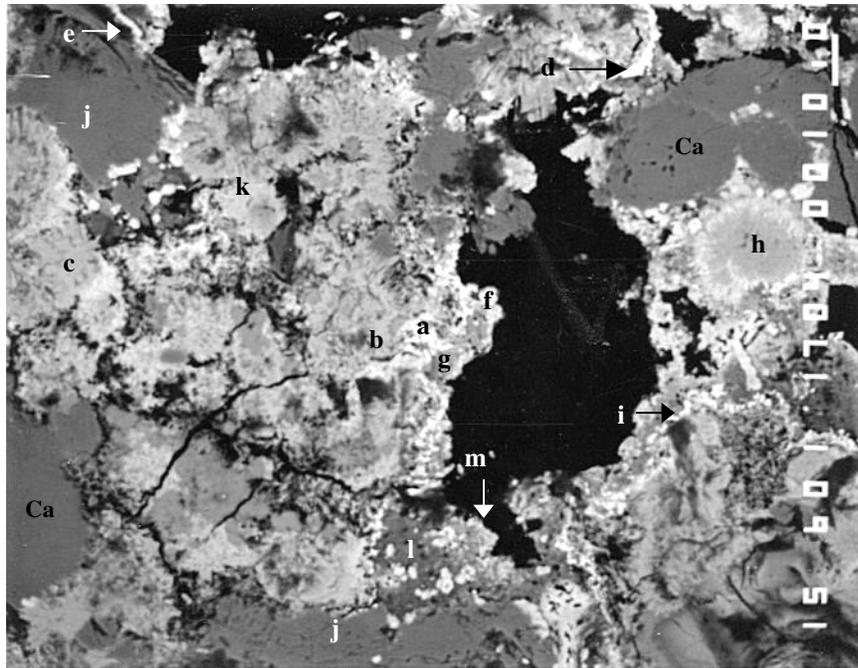
White bar = 10 μm   600 ×

Figure 8. COT-1-0 EM, Example 5

Spot	Weight, %						Description
	Ca	U	Mo	Fe	S	Si	
a	1.0	18	2.7	28	9	1.2	
b			0.2	57	0.1		
c			0.2	57	0.2		
d	0.86	21	1.4	40	19	1.1	White Band
e			0.4	51	26	3.7	White Band
f			0.3	51	24	2.5	
g			0.3	44	20	1.5	
h			0.1	57	0.5	1.5	
h (rim)		12	0.3	45	1.4	0.9	Light Rim on h
i	1.2	28	2.2	21	8	1.8	White Band
j	34			11			Both the Same
k			1.6	50	15	5.8	
l			0.4	38	16	2.1	
m			0.4	50	23	1.3	
Ca							CaCO$_3$

See the sulfur x-ray map in Figure 9.
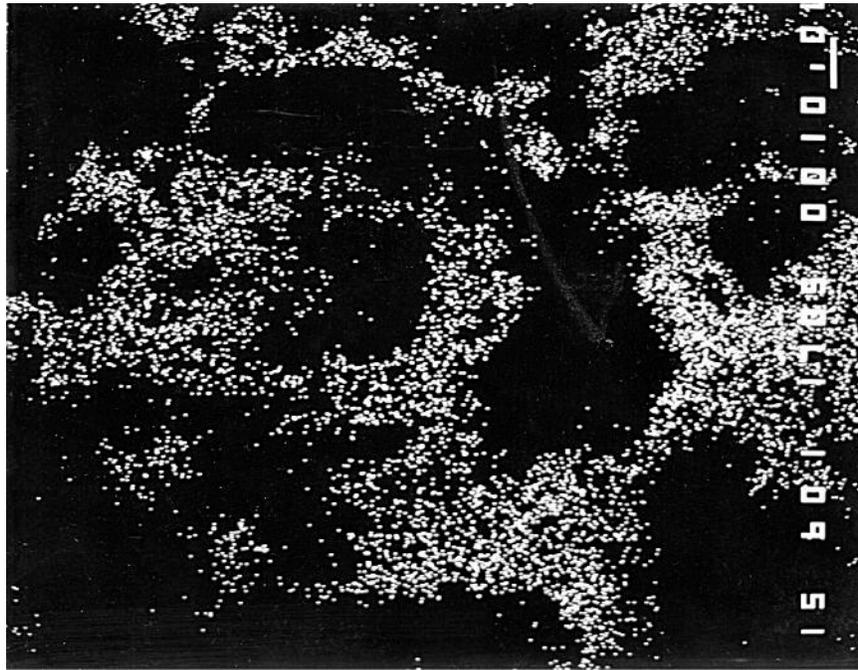
White Bar = 10 μm   600 ×

Figure 9. COT-1-0 EM, Sulfur Map of Figure 8

White Bar = 100 μm   300 ×
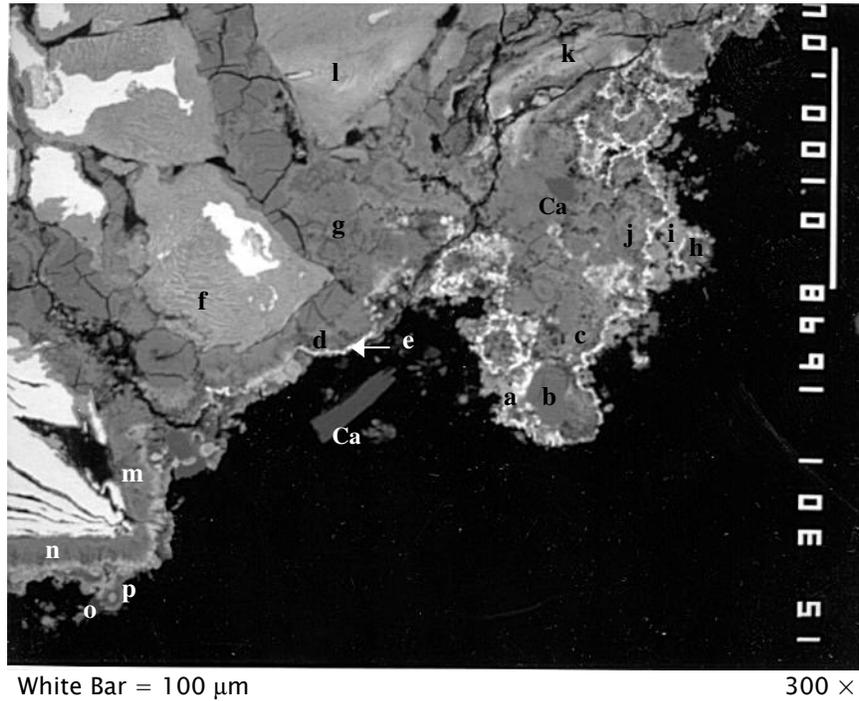
Figure 10. COT-1-0 EM, Example 6

Spot	Weight, %						Description
	Ca	U	Mo	Fe	S	Si	
a	0.7	31	0.46	25	5.8	5	White Area
b				38		17	
c		0.37	4.0	46	20	3.7	
d	1.0	3.0	3.9	38	15	2.1	Darker Area
e	1.5	26	1.2	18	6.9	1.9	
f	0.1	<0.1	0.5	60	2.6	3.9	
g	0.5	<0.1	0.1	55	0.1	0.3	
h	0.6	1.6	4.0	34	15	1.7	
i	0.1	0.41	0.3	51	26	0.6	
j	0.7	2.7	4.4	44	19	2.8	
k	0.7	0.1	5.6	49	5.9	4.7	
l	0.05	0.1	0.3	63	1.3	4.0	
m	0.2		0.3	47	0.4	13	
n	0.5	<0.1	0.2	54	0.14	0.8	Wide Dark Band
o	0.5	0.38	0.5	52	25	0.9	Outermost Light Band
p	0.8	18	0.2	42	1.2	1.0	Inner Light Band
Ca							$CaCO_3$ Darker Gray

The medium gray areas (f, g, l, and n) are probably hydrated iron oxide. See the uranium x-ray map in Figure 11, the sulfur x-ray map in Figure 12, and the calcium x-ray map in Figure 13.

White Bar = 100 μm   300 ×

Figure 11. COT–1–0 EM, Uranium Map of Figure 10

White Bar = 100 μm   300 ×

Figure 12. COT-1-0 EM, Sulfur Map of Figure 10

White Bar = 100 μm   300 ×

Figure 13. COT-1-0 EM, Calcium Map of Figure 10
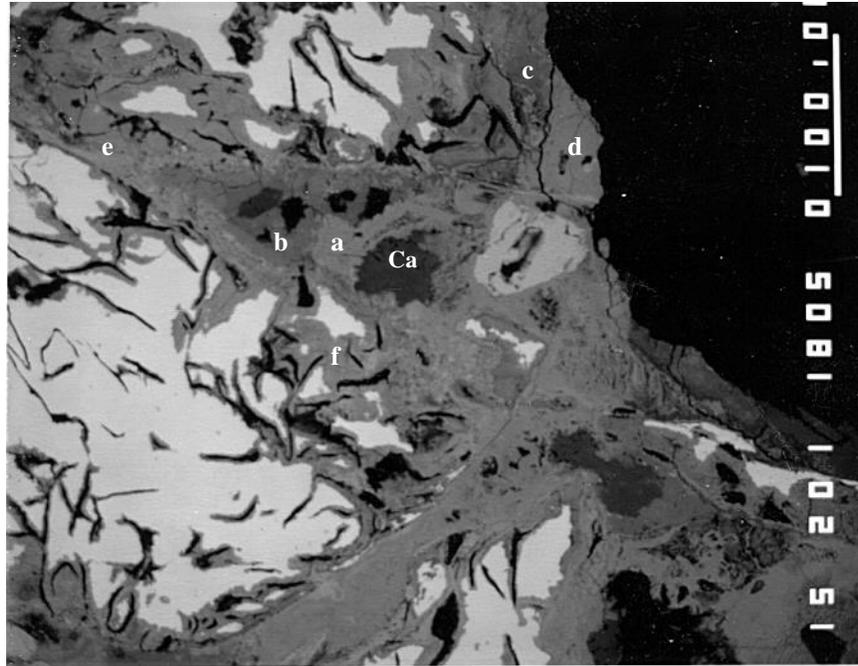
White Bar = 100 µm   200 ×

Figure 14. COT-1-5 EM, Example 1

Spot	Weight, %				Description
	Mo	Fe	S	Si	
a		67	0.10		
b	0.12	54	1.2		
c		54	6.9	4.1	
d		59	3.2	1.9	
e		59	15	1.5	
f	0.05	60	5.4	3.6	
Ca					CaCO₃

Sulfide sulfur is present, but at relatively low sulfur concentrations. The medium gray areas (a through d and f) are probably mostly hydrated iron oxide with local low levels of molybdenum.
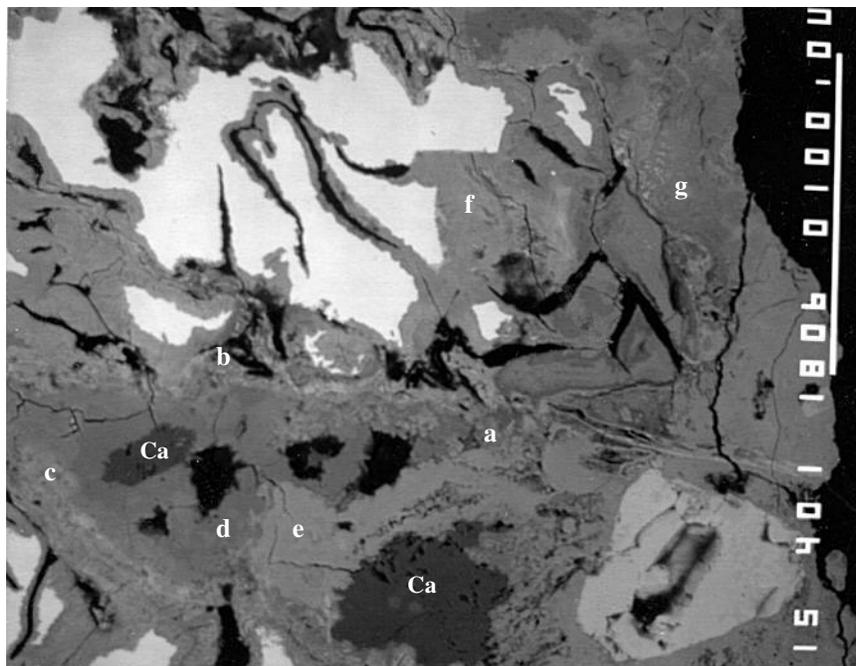
White Bar = 100 μm   400 ×

Figure 15. COT-1-5 EM, Example 2

Spot	Weight, %				Description
	Mo	Fe	S	Si	
a	<0.05	46	12	1.5	
b	<0.05	56	15	2.4	
c	<0.05	56	12	3.6	
d	<0.05	59	0.5		
e	<0.05	61	3.8	0.6	
f	0.07	59	3.4	5.8	
g	0.08	54	7.1	3.9	
Ca					CaCO$_3$

Low and moderate concentrations of sulfide sulfur are present, and occasional traces of molybdenum are present. See the sulfur x-ray map in Figure 16.
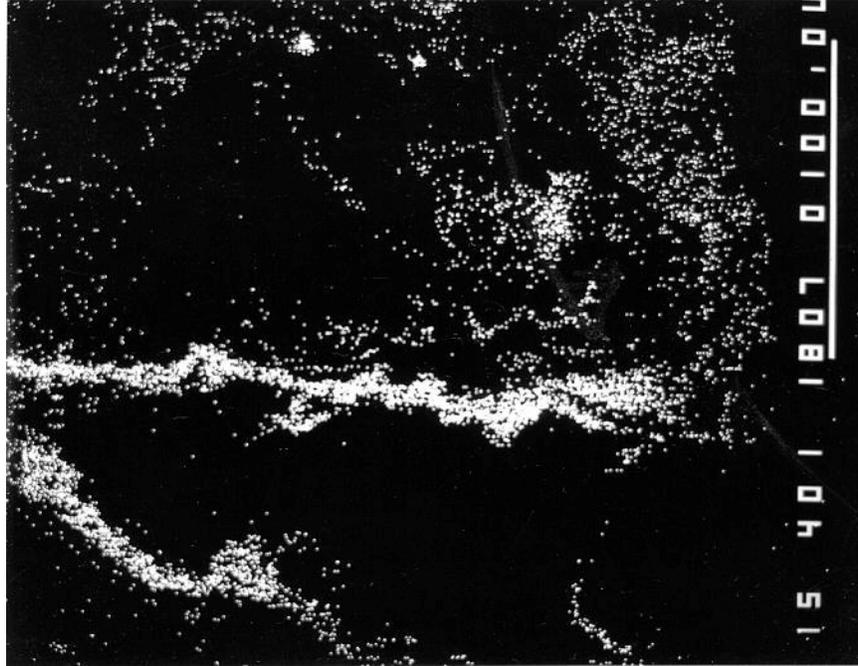
White Bar = 100 µm   400 ×

Figure 16. COT-1-5 EM, Sulfur Map of Figure 15
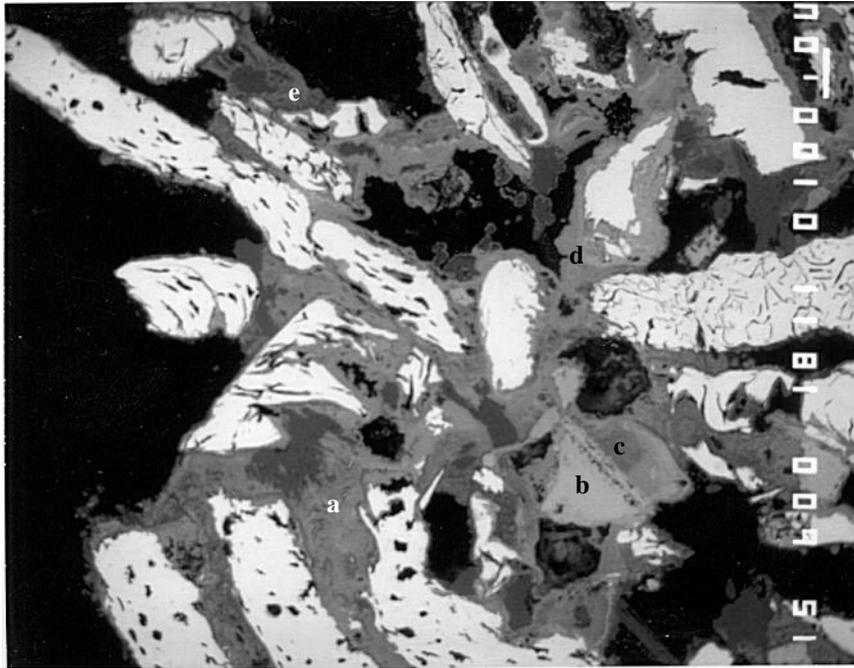
White Bar = 100 µm   60 ×

Figure 17. COT-1-5 EM, Example 3

Spot	Weight, %				Description
	Ca	Fe	S	Si	
a		64	0.3	0.2	
b		75			
c		57	0.4	1.8	
d		58	5.7	0.7	
e	4.3	54	0.11	0.4	

The medium gray areas (a, c, d, and e) are probably mostly hydrated iron oxide.
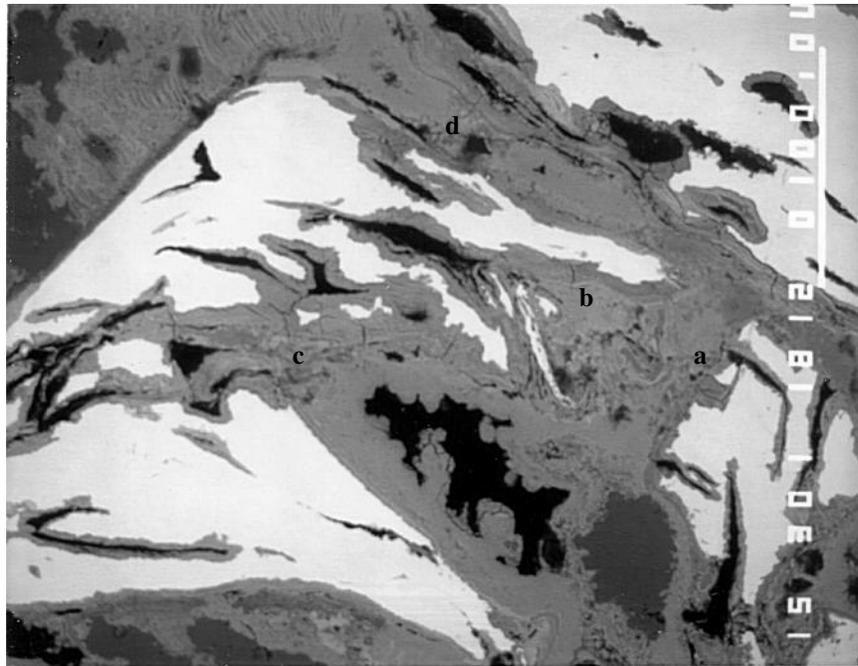
White Bar = 100 μm   300 ×

Figure 18. COT-1-5 EM, Example 4

Spot	Weight, %					Description
	Ca	Mo	Fe	S	Si	
a		0.08	58	19	0.9	
b			59	19	1.0	
c	0.24	0.13	56	16	2.6	
d			57	14	1.2	

The gray areas appear to be mostly hydrated iron oxide, but there are bands of iron sulfide in the areas analyzed. See the sulfur x-ray map in Figure 19.
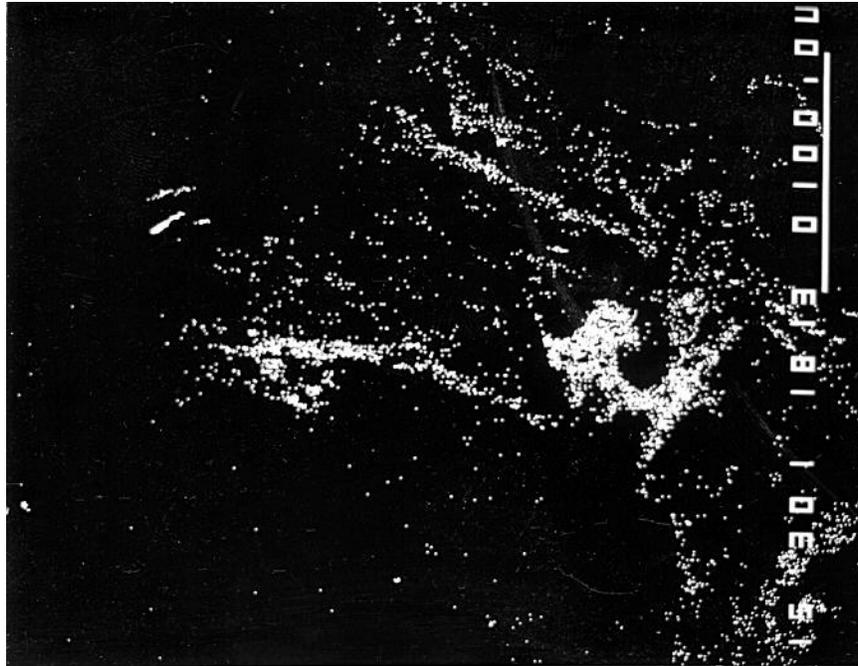
White Bar = 100 µm   300 ×

Figure 19. COT–1–5 EM, Sulfur Map of Figure 18
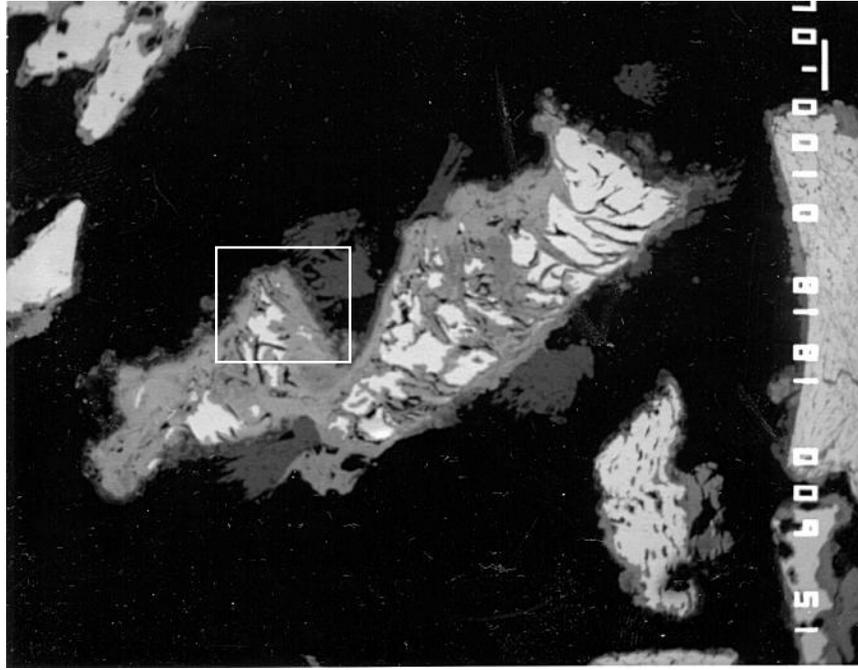
White Bar = 100 μm   60 ×

Figure 20. COT-1-5 EM, Example 5

Close-up of boxed area is shown in Figure 21.
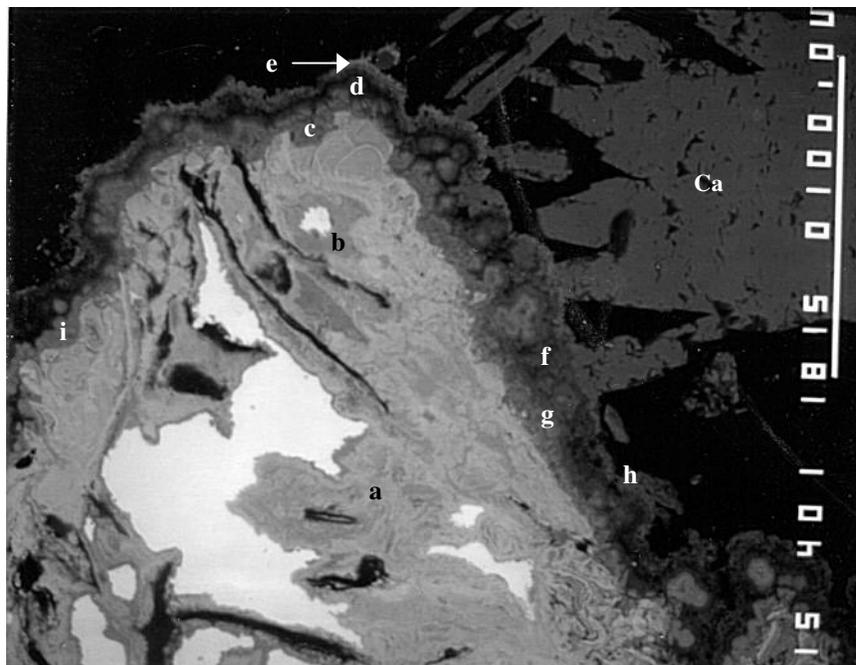
White Bar = 100 μm   400 x

Figure 21. COT-1-5 EM, Close-up of Boxed Area in Figure 20

Spot	Weight %				Description
	Ca	Fe	S	Si	
a		64	0.2	3.8	
b	0.03	61	0.4	1.0	
c	0.69	54	1.7	1.5	
d	0.81	39	1.1	1.4	
e	0.52	58	0.2	0.4	
f	0.71	33	1.7	1.1	
g	0.85	57	0.9	1.5	
h	27.6	7.4	0.3	2.6	
i	0.77	52	2.8	1.1	
Ca					$CaCO_3$

Mostly low-level sulfide is present in this area with some spotty higher levels, as indicated in Figure 22. The medium gray area is probably mostly hydrated iron oxide. See the sulfur x-ray map in Figure 22 and the calcium x-ray map in Figure 23.
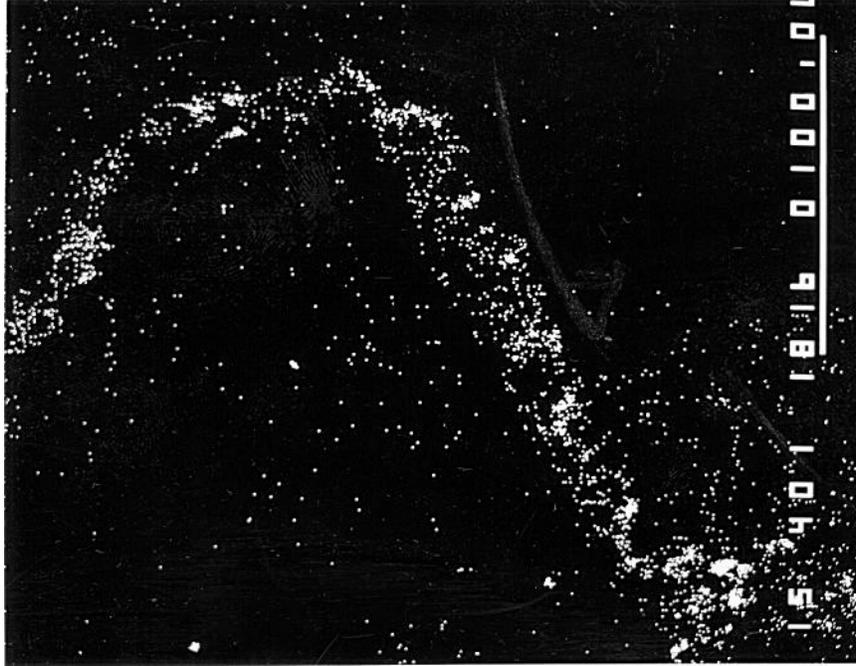
White Bar = 100 μm   400 ×

Figure 22. COT-1-5 EM, Sulfur Map of Figure 21

White Bar = 100 µm   400 ×

Figure 23. COT–1–5 EM, Calcium Map of Figure 21

White Bar = 100 µm   400 ×

Figure 24. COT-1-0.5 HCl EM, Example 1

This entire sample is similar to the areas shown in the photograph. The white areas are metallic iron. The fibrous gray material is relatively fine-grained and is possibly intermingled with carbon, making quantitative analysis uncertain. Very little oxygen is present, so the gray material could possibly be iron carbide. The analysis of this material is greater than 50% Fe, approximately 0.4% S, and approximately 1% Si.

White Bar = 10 μm   1,500 ×

Figure 25. COT-1-0.5 HCl EM, Example 2

This is a secondary electron image of an area similar to that in Figure 24. The dark gray stringers are carbon, evidently graphite.
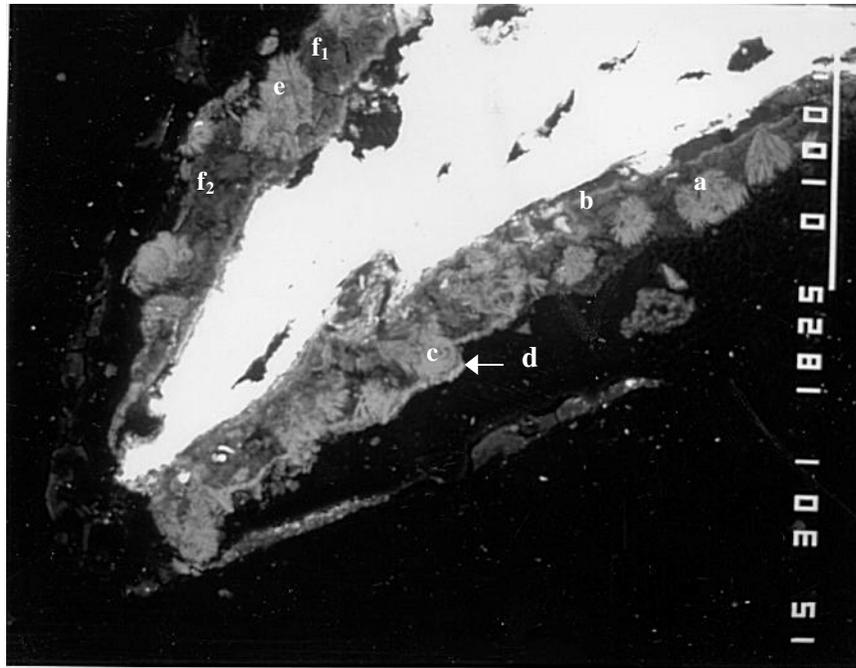
White Bar = 100 μm   300 ×

Figure 26. COT-1-2.5 EM, Example 1

Spot	Weight, %					Description
	Ca	Mo	Fe	S	Si	
a		0.16	55	0.15		
b		0.03	29	3.6	1.6	
c	0.3	0.11	53	0.06	0.03	
d	0.37	0.27	59	0.65	2.0	
e	0.23	0.25	58	0.25	0.44	
f_1		0.12	33	6.7	1.1	
f_2		0.10	29	6.5	1.7	

See the sulfur x-ray map in Figure 27.
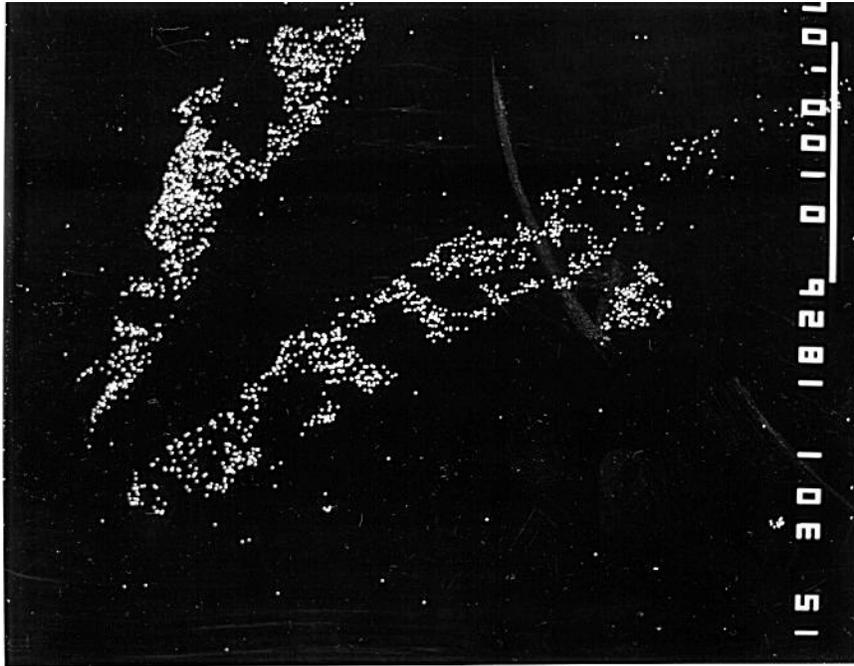
White Bar = 100 µm   300 ×

Figure 27. COT–1–2.5 EM, Sulfur Map of Figure 26
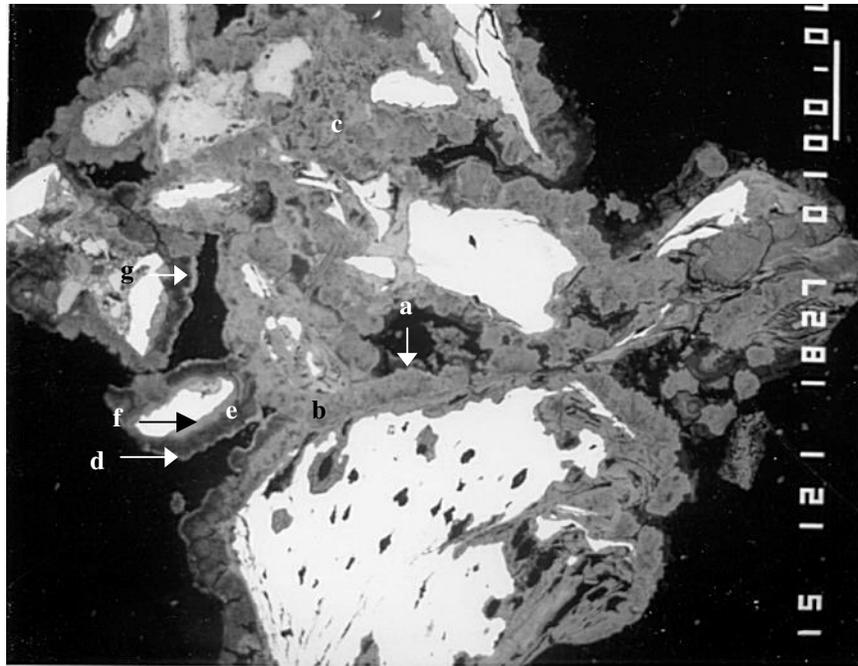
White Bar = 100 µm   120 ×

Figure 28. COT–1–2.5, Example 2

Spot	Weight, %				Description
	Mo	Fe	S	Si	
a	0.29	55	3.5	0.24	Slightly Lighter Rim
b	0.29	58	0.27		
c	0.27	58	0.64		
d		60	13.9		
e	0.07	33	5.6		Darker Gray
f	0.12	60	1.5		
g	0.04	59	17.7		Light Rim at the Right

The gray areas (a, b, c, and f) are probably hydrated iron oxide.
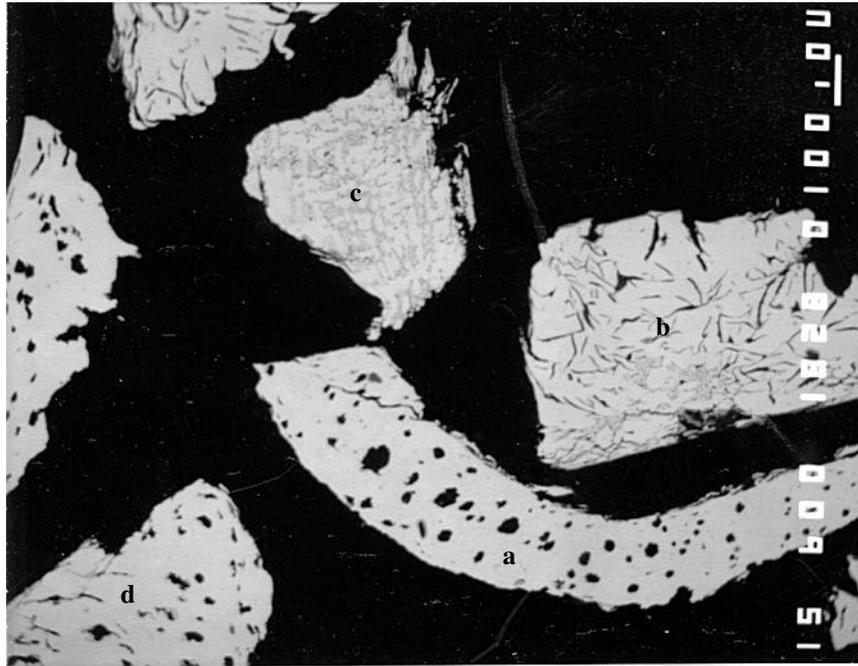
White Bar = 100 µm   60 ×

Figure 29. PEER EM

Particle	Weight, %	
	Fe	Si
a	97.0	2.6
b	97.2	2.2
c	97.4	2.1
d	98.2	2.5

Backscatter image showing metallic iron with inclusions of carbon.

Hydraulic Conductivity ASTM D5084

WESTERN COLORADO TESTING, INC.

Job Name: Iron Filing Filters   Job No.: 304505   Technician: BJR   Date: 2/11/2005
Sample Location: Lot 2.0-2.5   Depth: N/A   Lab Number: 05-121
Description: Cemented Iron Filings (Cored)

MDD (pcf): N/A   OMC (%): N/A   DD (pcf): 184.4   MC (%): 13.6   % Comp: N/A
Compaction Method: N/A   Test Method: C (Falling Head/Rising Tail)

Sample Height, intial/final (in)

	initial	final
#1	1.49	1.49
#2	1.56	1.56
#3	1.49	1.49
#4	1.42	1.42
Average	1.49	1.49

Sample Diameter, initial/final (in)

	initial	final
Top	1.87	1.87
Middle	1.87	1.87
Bottom	1.87	1.87
Average	1.87	1.87

Initial Wet Mass (g): 224.3

Moisture

	Initial	Final
Tare#	53	53
Tare Mass (g)	155.2	155.2
Tare and Wet (g)	379.5	379.5
Tare and Dry (g)	352.7	352.7

B-Coefficient

Cell Volume (cc)	Initial Cell Pressure (psi)	Final Cell Pressure (psi)	Initial Pore Pressure (psi)	Final Pore Pressure (psi)	Base Volume (cc)	Top Volume (cc)	B
---	30.9	40.9	30.0	39.5	---	---	95

Temp (C) = 19.1
a_{in} (m^2) = 1.97E-05
a_{out} (m^2) = 1.97E-05
L (m) = 3.78E-02
A (m^2) = 1.77E-03
R_T = 1.030
k** (m/s) = 1.2E-05
k_{20} (m/s) = 1.3E-05   (1.3E-3 cm/s)
Void Ratio: 0.40
Pore Volume (cc): 26.80
Volume Flowed (cc): 111.60
Pore Volumes Flowed: 4.2
Back Pressure* (psi): 40.0
Confining Pressure* (psi): 1.0
Max. Stress (psi): 1.2   Min. Stess (psi): 0.8

Hydraulic Conductivity

Elapsed Time (sec)	Cell Pressure (psi)	Base Pressure (psi)	Top Pressure (psi)	Base Volume (cc)	Top Volume (cc)	Head Loss, h_1 (m)	Head Loss, h_2 (m)	Conductivity, k (m/s)	Hydraulic Gradient
0	40.9	40.1	39.9	0.20	9.99				
30	40.9	40.1	39.9	4.44	5.21	0.638	0.180	8.88E-06	5
60	40.9	40.1	39.9	5.75	4.45	0.180	0.075	6.15E-06	2
90	40.9	40.1	39.9	6.21	4.01	0.075	0.029	6.67E-06	1
0	41.1	40.0	40.0	3.10	9.88				
15	41.1	40.0	40.0	4.66	8.06	0.344	0.173	9.65E-06	5
30	41.1	40.0	40.0	5.51	7.29	0.173	0.090	9.17E-06	2
45	41.1	40.0	40.0	5.98	6.78	0.090	0.041	1.10E-05	1
60	41.1	40.0	40.0	6.24	6.53	0.041	0.015	1.41E-05	0.4
75	41.1	40.0	40.0	6.35	6.44	0.015	0.005	1.54E-05	0.1

*Average for duration of test.   **Average for last four readings.

Remarks: Pore Volume estimated from final moisture content.

Fig. HC-2

WESTERN COLORADO TESTING, INC.

Hydraulic Conductivity ASTM D5084

Job Name: Iron Filing Filters Job No.: 304505 Technician: JCH Date: 2/7/2005

Sample Location: Lot 7.0-2.5 Depth: N/A Lab Number: 05-120

Description: Cemented Iron Filings (Cored)

MDD (pcf): N/A OMC (%): N/A DD (pcf): 159.8 MC (%): 17.9 % Comp: N/A

Compaction Method: N/A Test Method: C (Falling Head/Rising Tail)

Sample Height, intial/final (in)		
#1	1.64	1.64
#2	1.57	1.57
#3	1.62	1.62
#4	1.64	1.64
Average	1.62	1.62

Sample Diameter, initial/final (in)		
Top	1.92	1.92
Middle	1.93	1.93
Bottom	1.93	1.93
Average	1.93	1.93

Initial Wet Mass (g): 233.2

Moisture	Initial	Final
Tare#	S2	S2
Tare Mass (g)	156.1	156.1
Tare and Wet (g)	389.3	389.3
Tare and Dry (g)	353.9	353.9

B-Coefficient

Cell Volume (cc)	Initial Cell Pressure (psi)	Final Cell Pressure (psi)	Initial Pore Pressure (psi)	Final Pore Pressure (psi)	Base Volume (cc)	Top Volume (cc)	B
---	31.3	41.3	29.8	39.3	---	---	95

Hydraulic Conductivity

Elapsed Time (sec)	Cell Pressure (psi)	Base Pressure (psi)	Top Pressure (psi)	Base Volume (cc)	Top Volume (cc)	Head Loss, h_1 (m)	Head Loss, h_2 (m)	Conductivity, k (m/s)	Hydraulic Gradient
0	41.3	40.3	39.0	0.24	9.59				
30	41.3	40.3	39.0	8.97	1.04	1.389	0.511	7.17E-06	12
0	41.3	40.3	40.2	0.13	9.89				
30	41.3	40.3	40.2	3.23	6.72	0.566	0.248	5.92E-06	6
60	41.3	40.3	40.2	4.54	5.43	0.248	0.116	5.45E-06	3
90	41.3	40.3	40.2	5.05	4.95	0.116	0.065	4.15E-06	2
120	41.3	40.3	40.2	5.24	4.79	0.065	0.047	2.33E-06	1
150	41.3	40.3	40.2	5.36	4.67	0.047	0.035	2.11E-06	1
180	41.3	40.3	40.2	5.38	4.65	0.035	0.033	4.22E-07	1
0	41.3	40.3	40.2	1.06	9.79				
30	41.3	40.3	40.2	3.79	6.96	0.514	0.231	5.74E-06	6
60	41.3	40.3	40.2	4.85	5.92	0.231	0.125	4.40E-06	3
90	41.3	40.3	40.2	5.20	5.60	0.125	0.091	2.28E-06	2
120	41.3	40.3	40.2	5.42	5.38	0.091	0.068	2.09E-06	2
150	41.3	40.3	40.2	5.57	5.23	0.068	0.053	1.79E-06	1
180	41.3	40.3	40.2	5.69	5.11	0.053	0.041	1.84E-06	1

Temp (C) = 18.5

a_{in} (m^2) = 1.97E-05

a_{out} (m^2) = 1.97E-05

L (m) = 4.11E-02

A (m^2) = 1.88E-03

R_T = 1.030

k** (m/s) = 2.0E-06

k_{20} (m/s) = 2.1E-06 (2.1E-4 cm/s)

Void Ratio: 0.46

Pore Volume (cc): 35.40

Volume Flowed (cc): 128.50

Pore Volumes Flowed: 3.6

Back Pressure* (psi): 40.2

Confining Pressure* (psi): 1.1

Max. Stress (psi): 2.3 Min. Stess (psi): 1.0

*Average for duration of test. **Average for last four readings.

Remarks: Pore Volume estimated from final moisture content.

Fig. HC-1

WESTERN COLORADO TESTING, INC.

Hydraulic Conductivity ASTM D5084

Job Name: Iron Filing Filters		Job No.: 304505	Technician: BJR	Date: 2/10/2005
Sample Location: Lot 0.0-0.5A		Depth: N/A		Lab Number: 05-122
Description: Cemented Iron Filings (Cored)				

MDD (pcf): N/A   OMC (%): N/A   DD (pcf): 162.0   MC (%): 12.9   % Comp: N/A

Compaction Method: N/A   Test Method: C (Falling Head/Rising Tail)

Sample Height, intial/final (in)		
#1	1.79	1.79
#2	1.83	1.83
#3	1.72	1.72
#4	1.82	1.82
Average	1.79	1.79

Sample Diameter, initial/final (in)		
Top	1.86	1.86
Middle	1.85	1.85
Bottom	1.83	1.83
Average	1.85	1.85
Initial Wet Mass (g):	230.0	

Moisture		
	Initial	Final
Tare#	10	10
Tare Mass (g)	172.8	172.8
Tare and Wet (g)	402.8	402.8
Tare and Dry (g)	376.6	376.6

B-Coefficient

Cell Volume (cc)	Initial Cell Pressure (psi)	Final Cell Pressure (psi)	Initial Pore Pressure (psi)	Final Pore Pressure (psi)	Base Volume (cc)	Top Volume (cc)	B
---	30.8	40.8	30.1	39.7	---	---	96

Temp (C) = 18.5

a_{in} (m^2) = 1.97E-05

a_{out} (m^2) = 1.97E-05

L (m) = 4.54E-02

A (m^2) = 1.73E-03

R_T = 1.030

k** (m/s) = 4.8E-06

k_{20} (m/s) = 5.0E-06   (5.0E-4 cm/s)

Void Ratio: 0.33

Pore Volume (cc): 26.20

Volume Flowed (cc): 131.25

Pore Volumes Flowed: 5.0

Back Pressure* (psi): 39.9

Confining Pressure* (psi): 1.0

Max. Stress (psi): 1.2   Min. Stess (psi): 0.9

Hydraulic Conductivity

Elapsed Time (sec)	Cell Pressure (psi)	Base Pressure (psi)	Top Pressure (psi)	Base Volume (cc)	Top Volume (cc)	Head Loss, h_1 (m)	Head Loss, h_2 (m)	Conductivity, k (m/s)	Hydraulic Gradiendt
0	40.9	39.9	39.8	0.37	9.40				
15	40.9	39.9	39.8	1.40	8.20	0.529	0.416	4.14E-06	9
30	40.9	39.9	39.8	2.90	6.70	0.416	0.263	7.89E-06	6
45	40.9	39.9	39.8	4.00	5.70	0.263	0.157	8.88E-06	3
60	40.9	39.9	39.8	4.70	5.00	0.157	0.086	1.04E-05	2
75	40.9	39.9	39.8	5.10	4.60	0.086	0.045	1.11E-05	1
90	40.9	39.9	39.8	5.35	4.30	0.045	0.017	1.68E-05	0
0	41.0	40.0	39.9	0.80	8.82				
15	41.0	40.0	39.9	2.50	7.30	0.478	0.314	7.23E-06	7
30	41.0	40.0	39.9	2.68	6.18	0.314	0.248	4.06E-06	5
45	41.0	40.0	39.9	4.40	5.46	0.248	0.124	1.19E-05	3
60	41.0	40.0	39.9	4.86	5.00	0.124	0.077	8.20E-06	2
75	41.0	40.0	39.9	5.16	4.72	0.077	0.048	8.13E-06	1
90	41.0	40.0	39.9	5.34	4.52	0.048	0.029	8.67E-06	1
105	41.0	40.0	39.9	5.46	4.42	0.029	0.017	9.19E-06	0
120	41.0	40.0	39.9	5.54	4.34	0.017	0.009	1.09E-05	0
0	41.0	40.0	39.9	0.22	9.60				
15	41.0	40.0	39.9	0.60	9.08	0.547	0.501	1.51E-06	11
30	41.0	40.0	39.9	2.30	7.38	0.501	0.328	7.29E-06	7
45	41.0	40.0	39.9	3.38	6.28	0.328	0.218	7.03E-06	5
60	41.0	40.0	39.9	4.08	5.69	0.218	0.152	6.21E-06	3
75	41.0	40.0	39.9	4.52	5.33	0.152	0.111	5.41E-06	2
90	41.0	40.0	39.9	4.82	4.83	0.111	0.071	7.69E-06	2
105	41.0	40.0	39.9	5.02	4.64	0.071	0.051	5.69E-06	1
120	41.0	40.0	39.9	5.14	4.52	0.051	0.039	4.62E-06	1
135	41.0	40.0	39.9	5.24	4.44	0.039	0.030	4.52E-06	1
150	41.0	40.0	39.9	5.30	4.37	0.030	0.023	4.57E-06	1

*Average for duration of test.   **Average for last four readings.

Remarks: Pore Volume estimated from final moisture content.